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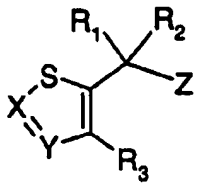
(54) Title: THIAZOLE–, ISOTHIAZOLE– AND THIADIAZOLE–DERIVATIVES HAVING MICROBICIDAL AND PLANT IMMUNIZING ACTIVITIES

(57) **Abstract**

Compounds of formula (I) and process for protecting and immunizing plants against attack by phytopathogenic microorganisms by applying compounds of formula (I) wherein a) X is CR_4 and Y is N; or b) X is N and Y is CR_5; or c) X and Y are N; and wherein Z is a C_1–group to which 1–3 halogen atoms or 1–3 unsubstituted or substituted hetero atoms selected from the group O, S and N are bonded; Z is CN, CO–A, CS–A or $CH(OR_{10})_2$; A is hydrogen, halogen, OR_6, SR_7, $N(R_8)R_9$, $ON(R_{11})R_{12}$ or $N(R_{13})OR_{14}$; and wherein R_1–R_{14} have the meanings given in the description.



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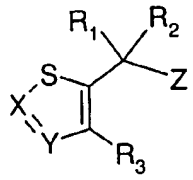
Thiazole-, isothiazole- and thiadiazole-derivatives having microbicidal and plant immunizing activities.

The invention relates to a method for protecting and immunizing plants against attack by phytopathogenic microorganisms by applying to the plants, to parts of the plants and/or to the locus of the plants a compound of formula I



I

wherein

a) X is CR_4 and Y is N; or

b) X is N and Y is CR_5; or

c) X and Y are N; and wherein

Z is a C_1-group to which 1-3 halogen atoms or 1-3 unsubstituted or substituted hetero atoms selected from the group O, S and N are bonded;

R_1 and R_2 are independently H, OH, SH, CN, COOH, NO_2, NH_2, halogen, C_1-C_6alkyl, haloC_1-C_6alkyl, alkoxyC_1-C_6alkyl, aminoC_1-C_6alkyl, alkoxaminoC_1-C_6alkyl, C_1-C_6alkoxy, halo-C_1-C_6alkoxy, C_1-C_6alkanoyloxy, aroyloxy, C_1-C_6alkoxycarbonyl, aryloxycarbonyl, benzyloxycarbonyl, C_1-C_6alkylcarbonyl, arylcarbonyl, benzylcarbonyl, aminocarbonyl, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl, C_1.C_6alkylthio, haloC_1-C_6alkylthio, C_1-C_6alkylsulfinyl, haloC_1-C_6alkylsulfinyl, C_1-C_6alkylsulfonyl, haloC_1-C_6alkylsulfonyl, arylsulfinyl, arylsulfonyl, C_2-C_6alkenyl, haloC_2-C_6alkenyl, C_2-C_6alkinyl, carboxyC_1-C_6alkyl, alkoxycarbonylC_1-C_6alkyl, haloalkoxycarbonylC_1-C_6alkyl, C_3-C_6cycloalkyl, alkanoylC_1-C_6alkyl, alkylcarbonyloxyC_1-C_6alkyl, phenylcarbonyloxyC_1-C_6alkyl, C_1-C_6alkylamino, C_1-C_6dialkylamino, C_2-C_6alkenylamino, C_1-C_6alkanoylamino, C_1-C_6alkoxycarbonylamino, benzylamino, benzoylamino, benzyloxyarbonylamino, phenyl, phenoxy, benzyl or phenethyl, wherein all the aromatic groups are unsubstituted or substituted from 1 to 5 substituents independently selected from halogen, hydroxy, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy and nitro; or optionally substituted heterocyclyl; or tri(C_1-C_6alkyl)silyl or tri(C_1-C_6alkyl)silyloxy;

with the proviso that R_1 and R_2 are not simultaneously a group selected from OH, SH, NO_2, NH_2, C_1-C_6alkylamino, C_1-C_6dialkylamino and C_2-C_6alkenylamino; or
R_1 and R_2 together are =O or =S; or
R_1 and R_2 together with the carbon atom to which they are bonded are an unsubstituted or substituted 3 to 8 membered isocyclic or heterocyclic ring; or
R_2 and Z together with the carbon atom to which they are bonded are an unsubstituted or substituted 3 to 7 membered lactone, lactame, thiolactone or thiolactame, which ring may have 1 to 2 additional hetero atoms selected from the group O, S and N;
R_3, R_4 and R_5 are independently H, OH, SH, CN, NO_2, NH_2, halogen, C_1-C_6alkyl, haloC_1-C_6alkyl, hydroxyC_1-C_6alkyl, alkoxyC_1-C_6alkyl, aminoC_1-C_6alkyl, alkoxaminoC_1-C_6alkyl, C_1-C_6alkoxy, C_1-C_6alkylthio, haloC_1-C_6alkylthio, C_1-C_6alkylsulfinyl, haloC_1-C_6alkylsulfinyl, C_1-C_6alkylsulfonyl, haloC_1-C_6alkylsulfonyl, halo-C_1-C_6alkoxy, C_2-C_6alkenyl, haloC_2-C_6alkenyl, C_2-C_6alkinyl, carboxyC_1-C_6alkyl, C_1-C_6alkanoyl, C_1-C_6alkoxycarbonyl, alkoxycarbonylC_1-C_6alkyl, haloalkoxycarbonylC_1-C_6alkyl, C_3-C_6cycloalkyl, alkanoylC_1-C_6alkyl, alkylcarbonyloxyC_1-C_6alkyl, phenylcarbonyloxyC_1-C_6alkyl, C_1-C_6alkylamino, C_1-C_6dialkylamino, C_2-C_6alkenylamino, C_1-C_6alkanoylamino, C_1-C_6alkoxycarbonylamino, benzylamino, benzoylamino, phenyl, phenoxy, benzyl or phenethyl, the phenyl rings of which are unsubstituted or substituted from 1 to 3 substituents independently selected from halogen, hydroxy, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy and nitro; or optionally substituted heterocyclyl.

The invention relates also to new compounds of formula I, to the preparation of those compounds, to new intermediates and to agrochemical compositions comprising at least one of those compounds as active ingredient.

Thiazole and thiadiazole derivatives having plant-fungicidal activities are known from EP-A-395,174, US 5,135,927, WO 96/17840, and WO 96/29871.
EP-A-757,987 and WO 97/20465 discloses thiazole and thiadiazole derivatives exhibiting plant immunizing activities. These compounds have no or very weak direct activity against fungi and bacteria, but protect the plants from phytopathogenic microorganisms by activation and stimulation of the plant's own defence system (immunisation). That mode of action has also become known by the name "Systemic Activated Resistance" ("SAR"). Such compounds and methods are ecologically advantageous and are complementary to current methods in crop protection. It is therefore desirable to provide more compounds and

methods for protecting plants by immunizing them against attack by phytopathogenic microorganisms.

Surprisingly it has now been found that compounds of formula I can be used for protecting and immunizing plants against attack by microorganisms, such as phytopathogenic fungi, bacteria and viruses and for improving the qualities of the plants.

The formula I embraces all stereoisomeric forms and mixtures thereof, such as enantiomeric and diastereomeric pure forms and mixtures thereof.
The compounds of formula I and, where appropriate, their tautomers can be in the form of salts. Compounds of formula I that have at least one basic centre can form acid addition salts. Furthermore, compounds of formula I having at least one acid group can form salts with bases. Preference is given to agrochemically advantageous salts.

Z is a C_1-group which means that no additional carbon atoms are directly attached to this group. Examples for the group Z are trihalomethyl, dihalomethyl or halomethyl as chloromethyl; formyl or an acetal or thioacetal thereof; a carboxylic acid or derivatives thereof, as nitrile, esters, anhydrides, thioesters, amides, amidines, imidic-,hydrazonic- and hydroxamic-acids or derivatives thereof; or heterocyclyl, as 2-imidazolyl, 2-pyrimidinyl and 2-thiazolyl.

Compounds of formula I wherein R_1 and R_2 are simultaneously a group selected from OH, SH, NO_2, NH_2, C_1-C_6alkylamino, C_1-C_6dialkylamino and C_2-C_6alkenylamino are not stable in general and are thus not part of this invention.

Unless defined otherwise, the general terms used hereinbefore and hereinafter have the meanings given below:
Hydrocarbon radicals may be saturated or unsaturated, open-chained or cyclic, or mixed open-chained and cyclic, for example cyclopropylmethyl or benzyl.
Alkyl groups are straight-chained or branched and are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, sec-amyl, tert-amyl, 1-hexyl or 3-hexyl.
Unsaturated hydrocarbon radicals are alkenyl, alkynyl or alkenynyl groups having not more than three multiple bonds, for example butadienyl, hexatrienyl or 2-penten-4-ynyl.

Alkenyl is straight-chained or branched alkenyl, for example allyl, methallyl, 1-methylvinyl or but-2-en-1-yl. Preference is given to alkenyl radicals having a chain length of 2 to 4 carbon atoms.

Alkynyl may be straight-chained or branched, for example propargyl, but-1-yn-1-yl or but-1-yn-3-yl. Propargyl is preferred.

Cyclic unsaturated hydrocarbon radicals may be aromatic, for example phenyl and naphthyl, or non-aromatic, for example cyclopentenyl, cyclohexenyl, cycloheptenyl and cyclooctadienyl, or partially aromatic, for example tetrahydronaphthyl and indanyl.

Halogen, or halo, is fluorine, chlorine, bromine or iodine, preferably fluorine, chlorine or bromine.

Haloalkyl may contain identical or different halogen atoms, for example fluoromethyl, difluoromethyl, difluorochloromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, 2,2,2-trichloroethyl, 3,3,3-trifluoropropyl.

Alkoxy is, for example, methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy and tert-butoxy, preferably methoxy and ethoxy.

Haloalkoxy is, for example, difluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 1,1,2,2-tetrafluoroethoxy, 2-fluoroethoxy, 2-chloroethoxy and 2,2-difluoroethoxy.

Cycloalkyl is cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.

Alkanoyl is either straight-chained or branched. Examples are formyl, acetyl, propionyl, butyryl, pivaloyl and octanoyl.

A heterocyclyl radical is to be understood as being a 3 to 7-membered, aromatic or non-aromatic ring having hetero atoms N, O and/or S. Furthermore, an unsubstituted or substituted benzo group may be fused onto such a heterocyclyl radical bonded to the rest of the molecule. Examples of heterocyclyl groups are pyridyl, pyrimidinyl, imidazolyl, thiazolyl, 1,3,4-thiadiazolyl, triazolyl, thienyl, furanyl, pyrrolyl, morpholinyl, oxazolyl and the corresponding partially or completely hydrogenated rings. Examples of heterocyclyl groups to which a benzo group is fused are quinolyl, isoquinolyl, benzoxazolyl, quinoxalinyl, benzothiazolyl, benzimidazolyl, indolyl and indolinyl.

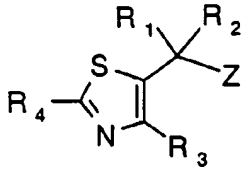
Aryl is phenyl, naphthyl, phenanthryl or fluorenyl, in particular phenyl.

The hydrocarbyl groups, as alkyl, alkenyl, alkynyl, and the haloalkyl, haloalkenyl, haloalkoxy and alkanoyl groups mentioned hereinabove and hereinbelow can be substituted by aryl,

hetaryl, aryloxy, hetaryloxy, arylsulfenyl, arylsulfinyl, arylsulfonyl, heterarylsulfenyl, hetarylsulfinyl or heterarylsulfonyl, each of which is unsubstituted or additionally substituted. All the aryl, hetaryl and heterocyclyl groups mentioned hereinabove and hereinbelow can be mono- or polysubstituted, for example by halogen, C_1-C_4alkyl, C_2-C_4alkenyl, C_2-C_4alkynyl, C_1-C_4alkoxy, C_1-C_4alkylthio, C_1-C_4haloalkyl, C_2-C_4haloalkenyl, C_2-C_4-haloalkynyl, C_1-C_4haloalkoxy, halogen, cyano, cyano-C_1-C_2alkyl, cyano-C_1-C_2alkoxy, OH, NO_2, SCN, thiocyanomethyl, $Si(CH_3)_3$, NH_2, $NH(C_1$-C_4alkyl), $N(C_1$-C_4alkyl)$_2$, C_1-C_4alkoxymethyl, C_1-C_4haloalkylcarbonyl, C_1-C_4haloalkyloxycarbonyl, C_1-C_4alkylcarbonyl, C_1-C_4-alkoxycarbonyl, aminocarbonyl, C_1-C_4alkylaminocarbonyl, bis(C_1-C_4alkylamino)carbonyl, arylaminocarbonyl, arylaminothiocarbonyl, C_1-C_4alkoximinomethyl, -$CSNH_2$, -SH, C_1-C_4alkylthiomethyl, C_2-C_4alkenyloxy, C_2-C_4alkynyloxy, C_2-C_4haloalkenyloxy, C_1-C_4alkylsulfinylmethyl, C_1-C_4alkylsulfonylmethyl, phenylsulfinylmethyl, phenylsulfonylmethyl, trifluoromethylsulfonyl, C_3-C_6cycloalkyl, C_1-C_4haloalkylcarbonyloxy, C_1-C_4alkylcarbonyloxy, C_1-C_4alkoxycarbonyloxy, haloalkoxycarbonyloxy, aminocarbonyloxy, C_1-C_4alkylaminocarbonyloxy, bis(C_1-C_4alkylamino)carbonyloxy, arylaminocarbonyloxy, arylaminothiocarbonyloxy.

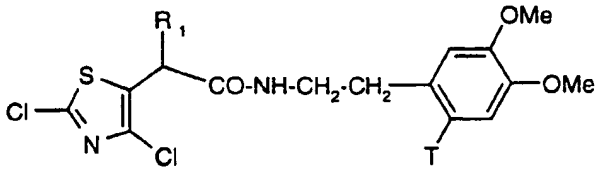
Amongst the compounds and methods of their use the following groups are preferred:

(1) Compounds of formula



I.A.

The compounds of the formula



wherein

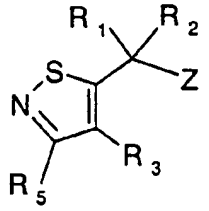
a) R_1 is $OCO-CH_3$ and T is Br,

b) R_1 is OH and T is Br,

c) R_1 is OH and T is H,

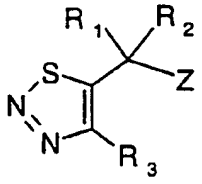
are known from WO 96/17840 as fungicides, but no indication is given therein to plant immunizing properties of these compounds ; these compounds are thus part of the invention only as far as the method for immunizing plants is concerned.

(2) Compounds of formula



I.B.

(3) Compounds of formula



I.C.

(4) Compounds of formula I, wherein

Z is CN, CO-A, CS-A or $CH(OR_{10})_2$;

A is hydrogen, halogen, OR_6, SR_7, $N(R_8)R_9$, $ON(R_{11})R_{12}$ or $N(R_{13})OR_{14}$;

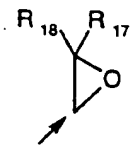
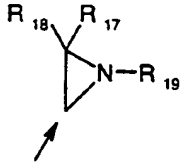
R_6 to R_{14} are independently hydrogen, an unsubstituted or substituted, open-chained, saturated or unsaturated hydrocarbon radical containing up to 8 carbon atoms, an unsubstituted or substituted, cyclic, saturated or unsaturated hydrocarbon radical containing up to 10 carbon atoms, unsubstituted or substituted benzyl or phenethyl, an unsubstituted or substituted acyl group containing up to 8 carbon atoms, an unsubstituted or substituted benzoyl group, or an unsubstituted or substituted heterocyclyl radical; or

R_8 and R_9, or R_{11} and R_{12}, together with the nitrogen atom to which they are bonded, form a 5- or 6-membered, unsubstituted or substituted heterocycle having 1 to 3 hetero atoms selected from O, S and/or N;
R_{10} are identical or different and are C_1-C_6alkyl that is unsubstituted or substituted by phenyl, C_1-C_2alkoxy, phenoxy or by benzyloxy; or
two substituents OR_{10}, together with the carbon atom to which they are bonded, form a cyclic acetal group that is unsubstituted or substituted by C_1-C_3alkyl, phenyl, benzyl, hydroxy or by C_1-C_3hydroxyalkyl.

(5) Compounds of formula I, wherein
Z is CO-A or CS-A;
A is OR_6, SR_7, $N(R_8)R_9$, $ON(R_{11})R_{12}$ or $N(R_{13})OR_{14}$;
R_6 to R_{14} are independently H, C_1-C_6alkyl, haloC_1-C_6alkyl, C_1-C_4alkoxycarbonyl, C_1-C_4alkanoylC_1-C_4alkyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkylmethyl, phenyl, benzyl, phenethyl, the phenyl rings of which are unsubstituted or substituted from 1 to 5 substituents independently selected from halogen, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy and C_1-C_2alkylenedioxy.

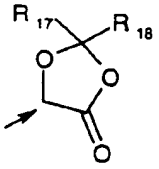
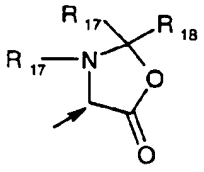
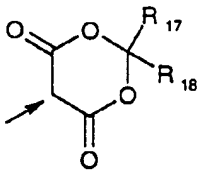
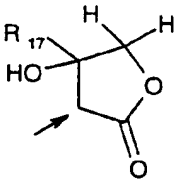
(6) Compounds of formula I, wherein
R_3 is H, OH, C_1-C_6alkyl, C_3-C_6cycloalkyl, haloC_1-C_6alkyl, C_1-C_6alkoxy or haloC_1-C_6alkoxy.

(7) Compounds of formula I, wherein
R_1 is H, OH, NH_2, halogen, COOH, C_1-C_4alkyl, haloC_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4alkanoyloxy, aroylyloxy, C_1-C_4alkoxycarbonyl, aryloxycarbonyl, benzyloxycarbonyl, C_1-C_4alkylcarbonyl, arylcarbonyl, benzylcarbonyl, aminocarbonyl, C_1-C_4alkylaminocarbonyl, C_1-C_4dialkylaminocarbonyl, alkanoylC_1-C_4alkyl, alkylcarbonyloxyC_1-C_4alkyl, C_2-C_4alkenyl, haloC_2-C_4alkenyl, C_1-C_4alkylamino, C_1-C_4dialkylamino, C_1-C_4alkanoylamino, C_1-C_4alkoxycarbonylamino, benzylamino, benzoylamino, phenyl, phenoxy, benzyl or phenethyl, the phenyl rings of which are unsubstituted or substituted from 1 to 3 substituents independently selected from halogen, hydroxy, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy and nitro;
R_2 is H, OH, C_1-C_4alkyl, C_1-C_4alkoxy or phenyl; or
R_1 and R_2 together are a group selected from

or

R_2+Z together are a group selected from

wherein R_{17}, R_{18} and R_{19} are independently H or C_1-C_4alkyl;

R_3 is H, halogen, C_1-C_6alkyl, haloC_1-C_6alkyl, C_3-C_6-cycloalkyl, C_1-C_4 alkoxycarbonyl, phenyl which is unsubstituted or substituted from 1 to 3 substituents independently selected from halogen, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy, amino, C_1-C_4alkylamino, C_1-C_4dialkylamino, benzylamino, C_1-C_4alkanoylamino, benzoylamino, C_1-C_4alkoxycarbonylamino, formyl, or a 4-7-membered cyclic or C_1-C_4alkyl open-chained acetal or thioacetal thereof;

R_4 is H, OH, halogen, amino, C_1-C_6alkyl, C_1-C_4alkylamino, C_1-C_4alkenylylamino, C_1-C_4dialkylamino, benzylamino, C_1-C_4alkanoylamino, benzoylamino, C_1-C_4alkoxycarbonylamino.

(8) Amongst group (7) those, wherein

R_3 is H, OH, halogen, C_1-C_6alkyl, haloC_1-C_6alkyl, C_3-C_6-cycloalkyl, C_1-C_6alkoxy, alkoxycarbonylC_1-C_6alkyl, phenyl, benzyl, the phenyl rings of which are unsubstituted or substituted from 1 to 3 substituents independently selected from halogen, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy and halo-C_1-C_2alkoxy; or formyl, or a 4-7-membered cyclic or C_1-C_4alkyl open-chained acetal or thioacetal thereof;

R_4 is H, OH, halogen, amino, C_1-C_6alkyl, C_1-C_4alkylamino, C_1-C_4alkenylylamino, C_1-C_4dialkylamino, benzylamino, C_1-C_4alkanoylamino, benzoylamino, or C_1-C_4alkoxycarbonylamino.

(9) Amongst group (6) those, wherein

Z is CO-A or CS-A;

A is hydrogen, halogen, OR_6, SR_7, $N(R_8)R_9$, $ON(R_{11})R_{12}$ or $N(R_{13})OR_{14}$;

R_6 to R_9 and R_{11} to R_{14} are independently hydrogen, an unsubstituted or substituted, open-chained, saturated or unsaturated hydrocarbon radical containing up to 8 carbon atoms, an unsubstituted or substituted, cyclic, saturated or unsaturated hydrocarbon radical containing up to 10 carbon atoms, unsubstituted or substituted benzyl or phenethyl, an unsubstituted or substituted acyl group containing up to 8 carbon atoms, an unsubstituted or substituted benzoyl group, or an unsubstituted or substituted heterocyclyl radical; or

R_8 and R_9, or R_{11} and R_{12}, together with the nitrogen atom to which they are bonded, form a 5- or 6-membered, unsubstituted or substituted heterocycle having 1 to 3 hetero atoms selected from O, S and/or N;

R_{10} are identical or different and are C_1-C_6alkyl that is unsubstituted or substituted by phenyl, C_1-C_2alkoxy, phenoxy or by benzyloxy; or

two substituents OR_{10}, together with the carbon atom to which they are bonded, form a cyclic acetal group that is unsubstituted or substituted by C_1-C_3alkyl, phenyl, benzyl, hydroxy or by C_1-C_3hydroxyalkyl.

(10) Amongst group (9) those, wherein

A is OR_6, SR_7, or $N(R_8)R_9$;

R_6, R_7, R_8 R_9 are independently H, C_1-C_6alkyl, haloC_1-C_6alkyl, C_1-C_4alkoxycarbonyl, alkoxycarbonylC_1-C_6alkyl, C_1-C_4alkanoylC_1-C_4alkyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkylmethyl, phenyl, benzyl, or phenethyl, the phenyl rings of which are unsubstituted or substituted from 1 to 3 substituents independently selected from halogen, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy.

(11) Amongst group (9) those, wherein

Z is CO-A;

A is OR_6 or $N(R_8)R_9$;

R_1 is H, OH, halogen, C_1-C_4alkyl, haloC_1-C_4alkyl, C_1-C_4alkoxy, halo-C_1-C_4alkoxy, amino, C_1-C_4alkylamino, C_1-C_4dialkylamino, benzylamino; phenyl, benzyl, or phenethyl, the phenyl rings of which are unsubstituted or substituted from 1 to 2 substituents independently selected from halogen, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy;

R_2 is H, OH, halogen, C_1-C_4alkyl, haloC_1-C_6alkyl, or phenyl,

R_3 is H, OH, C_1-C_6alkyl, C_3-C_6cycloalkyl, haloC_1-C_6alkyl, C_1-C_6alkoxy or haloC_1-C_6alkoxy,

R_4 is H or Cl,

R_6, R_8 and R_9 are independently H, C_1-C_6alkyl, haloC_1-C_6alkyl, C_1-C_6alkoxy, haloC_1-C_6alkoxy, C_1-C_4alkoxycarbonyl, C_1-C_4alkanoylC_1-C_4alkyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkylmethyl, phenyl, benzyl, or phenethyl, the phenyl rings of which are unsubstituted or substituted from 1 to 3 substituents independently selected from halogen, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy.

(12) Amongst group (11) those, wherein

R_1 is H, OH, halogen, C_1-C_4alkyl;

R_2 is H.

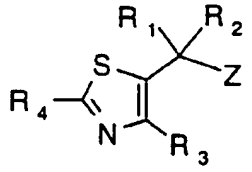
R_3 is H, cyclopropyl or CF_3,

R_4 is Cl.

(13) Amongst group (9) those, wherein

R_3 is H, halogen, C_1-C_4alkyl, haloC_1-C_4alkyl, C_3-C_6-cycloalkyl, C_1-C_4 alkoxycarbonyl, formyl, or a 4-7-membered cyclic or C_1-C_4alkyl open-chained acetal or thioacetal thereof.

(14) Compounds of formula



I.A

Z is CO-A;

A is hydrogen, OR_6, SR_7, $N(R_8)R_9$;

R_1 is H, OH, halogen or C_1-C_4alkyl,

R_2 is H;

R_3 is H, OH, C_1-C_6alkyl, C_3-C_6cycloalkyl, haloC_1-C_6alkyl, C_1-C_6alkoxy, haloC_1-C_6alkoxy, formyl, or a 4-7-membered cyclic or C_1-C_4alkyl open-chained acetal or thioacetal thereof;

R_4 is Cl;

R_6, R_7, R_8 and R_9 are independently H, C_1-C_6alkyl, haloC_1-C_6alkyl, C_1-C_6alkoxy, haloC_1-C_6alkoxy, C_1-C_4alkoxycarbonyl, C_1-C_4alkanoylC_1-C_4alkyl, C_3-C_6cycloalkyl,

C_3-C_6cycloalkylmethyl, phenyl, benzyl, or phenethyl, the phenyl rings of which are unsubstituted or substituted from 1 to 3 substituents independently selected from halogen, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy.

(15) Amongst group (14) those, wherein

A is OR_6 or SR_7;

R_1 and R_2 are H;

R_3 is C_1-C_6alkyl, C_3-C_6cycloalkyl, CF_3 or formyl;

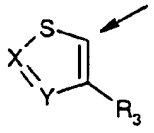
R_4 is Cl;

R_6 and R_7 are independently H, C_1-C_6alkyl, phenyl, benzyl, or phenethyl, the phenyl rings of which are unsubstituted or substituted with 1 to 2 substituents independently selected from halogen, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy and halo-C_1-C_2alkoxy.

Also preferred are the compounds of the tables.

The compounds of formula I may be prepared as outlined in the following reaction schemes.

Abbreviations:

Het: 

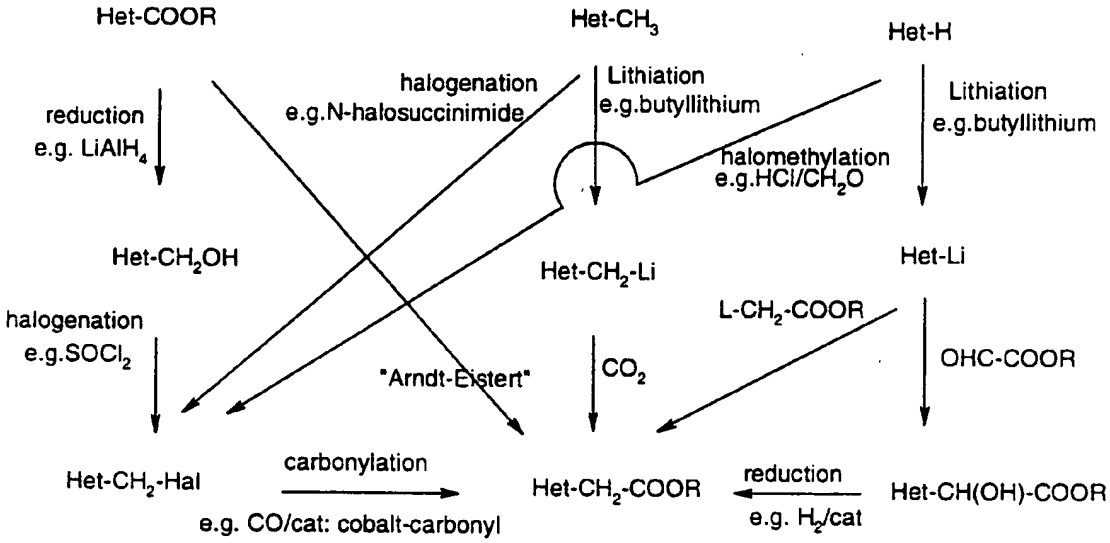
position to which the rest of the molecule is attached

Hal: halogen

L: leaving group, preferably chlorine, bromine, mesylate or tosylate.

R: a group which is inert under the reaction conditions

Scheme 1

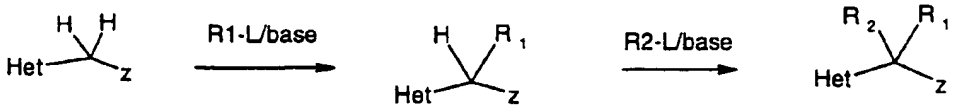


Of particular importance is the reaction step

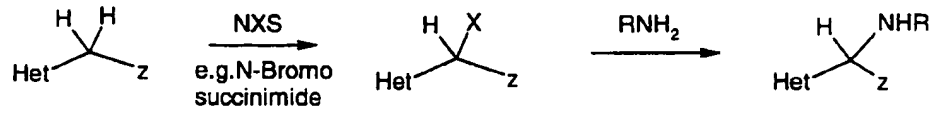
II.1 I.1

wherein X, Y and R_3 are as defined for formula I,
which comprises reaction of a compound of formula II.1 with carbon monoxide under pressure of 2-20 bars, preferably 5-10 bars, in presence of a catalyst, for example cobalt carbonyl and optionally a phase transfer catalyst.

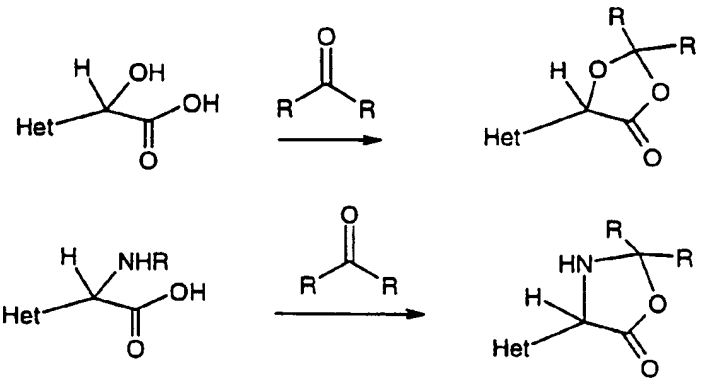
Scheme 2



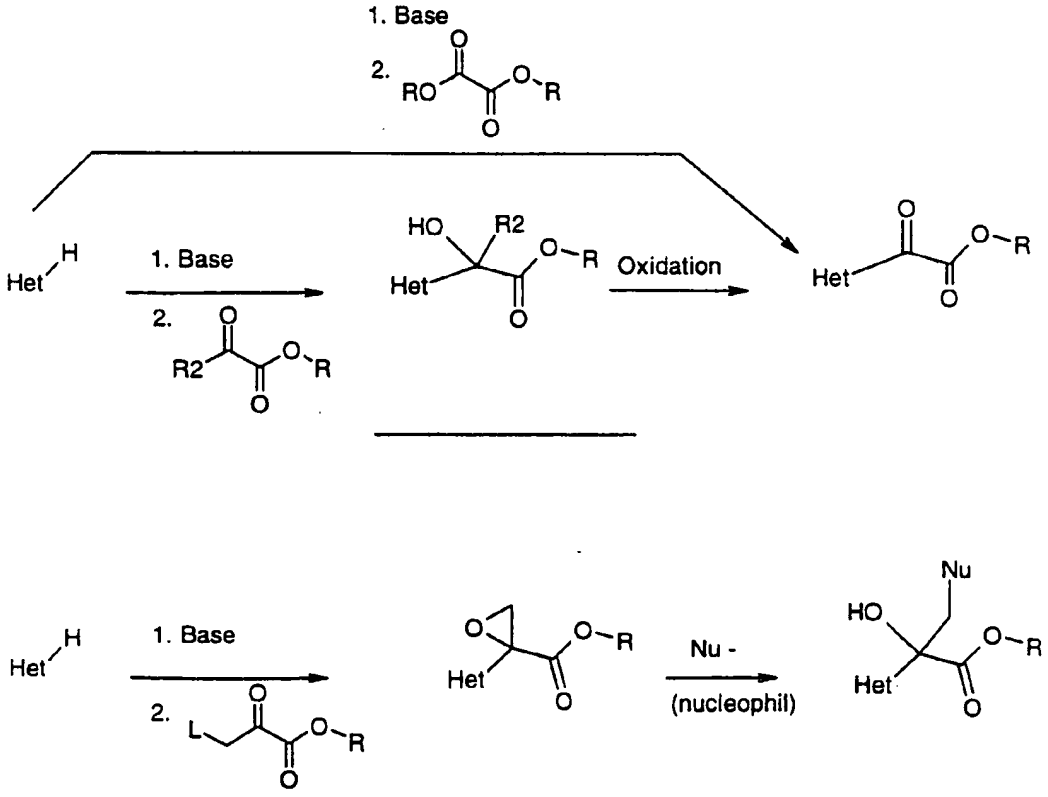
Scheme 3



Scheme 4

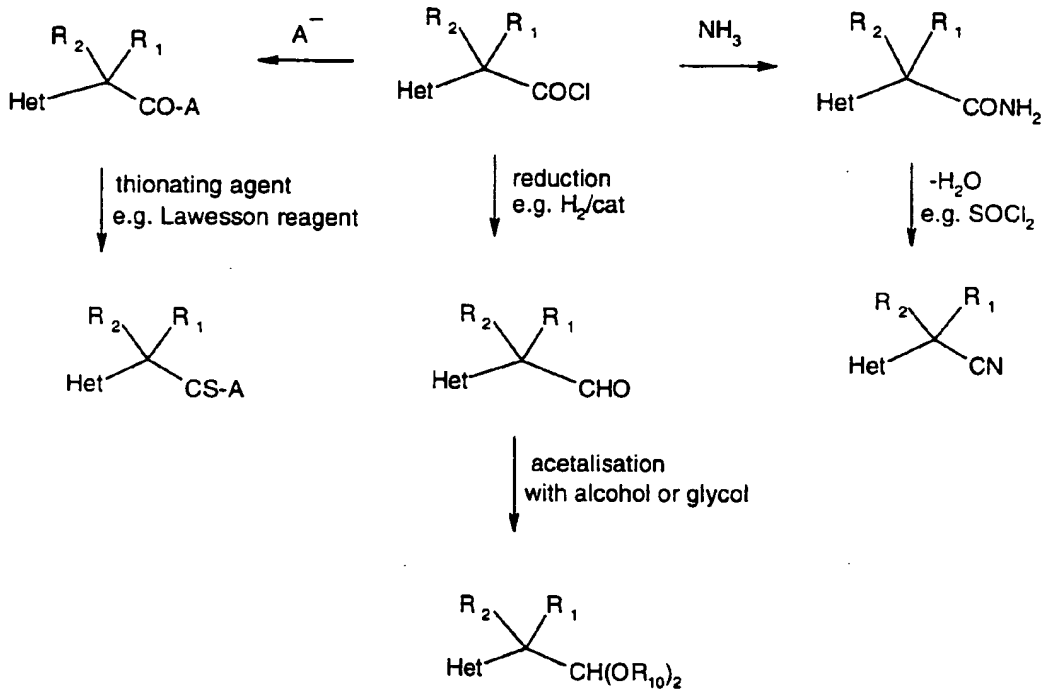


Scheme 5



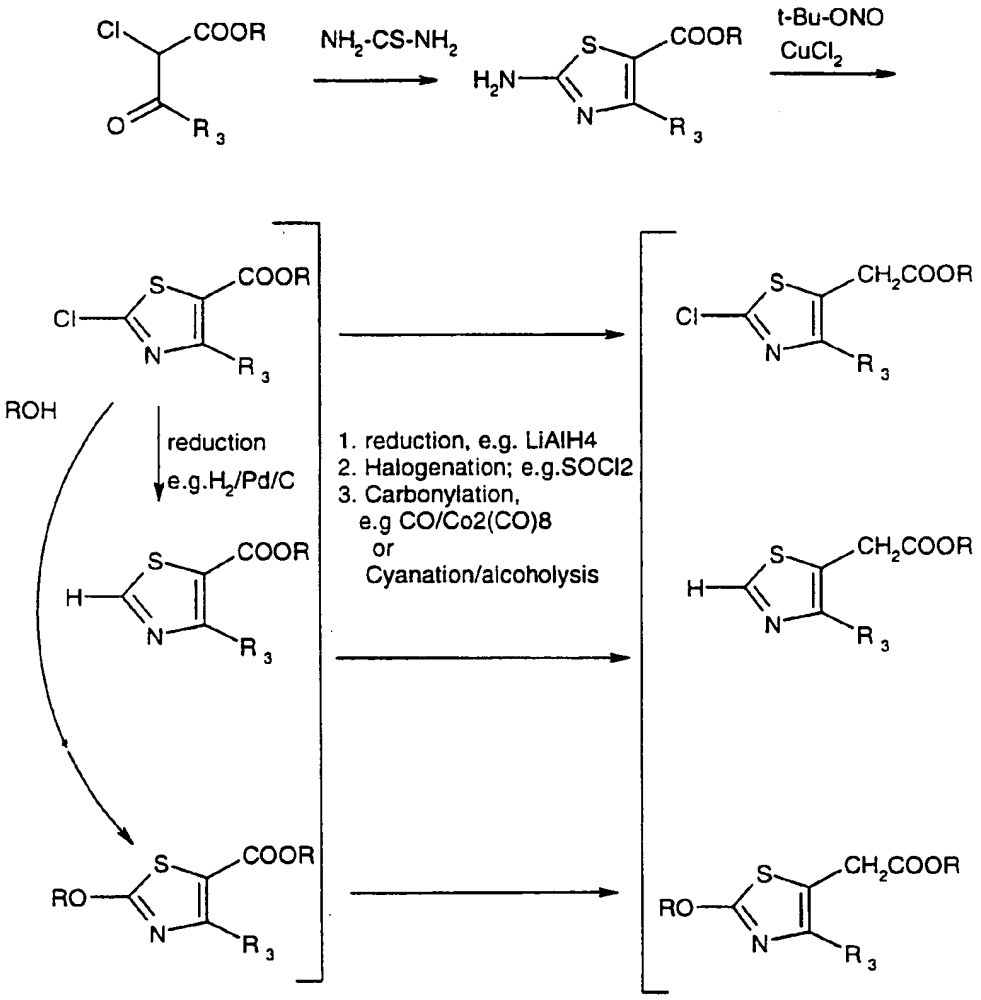
The functional groups of the compounds of formula I can be converted by known methods. For example, carboxylic acid derivatives can be converted as follows:

Scheme 6

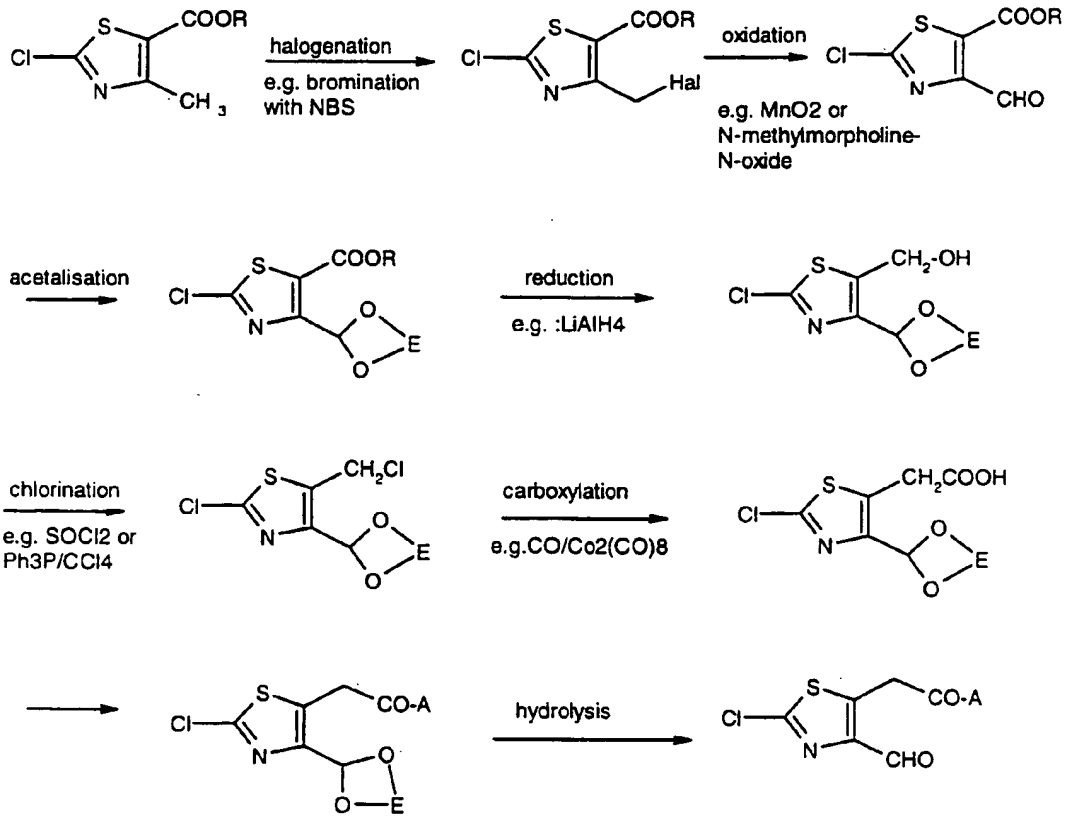


Of importance are the syntheses of schemes 7 and 8

Scheme 7

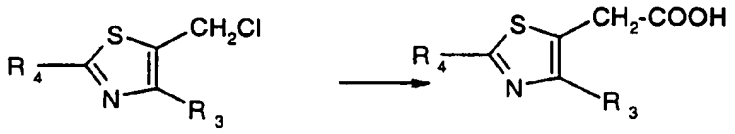


Scheme 8



E: optionally substituted C_2-C_5methylene

Of particular importance is the reaction step



II.A.1 I.A.1

which comprises reaction of a compound of formula II.A.1 with carbon monoxide under pressure of 2-20 bars, preferably 5-10 bars, in presence of a catalyst, for example cobalt carbonyl and optionally a phase transfer catalyst.

Particularly preferred is this reaction with compounds wherein R_3 is C_1-C_6alkyl, CF_3 or an acetal group, and R_4 is Cl.
Suitable bases, leaving groups, solvents and catalysts are known to the skilled person.

The thiazoles, isothiazoles and thiadiazoles can be synthesized by known methods or in analogy thereto according to the following references:

1.1 1,3-Thiazoles

Ahluwalia V. K. et *al*, *Heterocycles*, **32**, (1991), 907.
Fukatsu H. et *al*, *Heterocycles*, **29**, (1989) 1517.
Byers J. R.et *al*, *Org. Synthesis II*, (1943) 31.

1.2 1,2-Isothiazoles

R. G. Micetich, *Can J. Chem.*; (1970), **48**, 2006.
Adams A., Slack, *J. Chem. Soc.* (1959) 3061.
Buttimore D. et *al*, *J. Chem. Soc.* (1963) 2032.
Wooldrige K.R.H. *Adv. Het. Chem.* (1972), **14**, 1.

1.3 1,2,3-Thiadiazoles

Hurd C. D., Mori E. J., *J. Am. Chem. Soc.*, (1995), 5359.
Rämsky S. I. et *al.*, *Acta Pharm. Suecica* **10**, (1973), 285.
Scheitauer S., Mayer R. *Chem. Ber.* **100**, (1967), 1413.
R. Raap, Can. J. Chem. (1968), **46**. 2255.

The compounds of the invention can be used in the agricultural sector and related fields preventively and/or curatively. Besides their microbicidal properties, the compounds exhibit plant immunizing properties, i.e. plants can be protected by activation and stimulation of the plant's own defense system (immunization) which is known as "Systemic Activated Resistance" ("SAR").
Accordingly, with the compounds and methods of the invention, it is possible to control plant diseases on the one hand by strengthening the plant by activating its own defence system and on the other hand by additionally controlling the pathogens directly. The compounds offer a long lasting protection against a variety of pathogenes in different crops.

The compounds I can also be used as dressings in the treatment of seed (fruit, tubers, grains) and plant cuttings to provide protection against fungus infections as well as against phytopathogenic fungi which occur in the soil.

The compounds I are effective, for example, against phytopathogenic fungi belonging to the following classes: Fungi imperfecti (e.g. Botrytis, Pyricularia, Helminthosporium, Fusarium, Septoria, Cercospora and Alternaria) and Basidiomycetes (e.g. Rhizoctonia, Hemileia, Puccinia). Moreover, they are effective against the classes of the Ascomycetes (e.g. Venturia and Erysiphe, Podosphaera, Monilinia, Uncinula) and Oomycetes (e.g. Phytophthora, Pythium, Plasmopara).

Target crops to be protected within the scope of the present invention comprise e.g. the following species of plants: cereals (wheat, barley, rye, oats, rice, maize, sorghum and related species); beet (sugar beet and fodder beet); pomes, stone fruit and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soybeans); oil plants (rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans, groundnuts); cucumber plants (marrows, cucumber, melons); fibre plants (cotton, flax, hemp, jute); citrus fruit (oranges, lemons, grapefruit, mandarins); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika); lauraceae (avocados, cinnamon, camphor); and plants such as tobacco, nuts, coffee, aubergines, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as ornamentals.

The compounds I are generally used in the form of compositions and can be applied to the crop area or plant to be treated, simultaneously or in succession, with further compounds. These further compounds can be, for example, fertilisers or micronutrient donors or other preparations that influence plant growth. They can also be selective herbicides as well as insecticides, fungicides, bactericides, nematicides, molluscicides or mixtures of several of these preparations, if desired together with further carriers, surfactants or other application-promoting adjuvants customarily employed in formulation technology.
Suitable solvents, carriers and adjuvants are known to the skilled person.

A preferred method of applying a compound of formula I, or an agrochemical composition comprising at least one of those compounds, is application to the leaves (foliar application). The frequency and rate of application depend upon the risk of infestation by the corresponding pathogen. The compounds I can, however, also penetrate the plant through the roots *via* the soil (systemic action) if the locus of the plant is impregnated with a liquid formulation or if the substances are introduced in solid form into the soil, e.g. in the form of granules (soil application). In paddy rice crops, such granules can be applied in metered amounts to the flooded rice field. In order to treat seed, the compounds I can, however, also be applied to the seeds (coating), either by impregnating the grains or tubers with a liquid formulation of the active ingredient, or by coating them with a solid formulation.

Advantageous rates of application are normally from 5 g to 2 kg of active ingredient (a.i.) per hectare (ha), preferably from 10 g to 1 kg a.i./ha, especially from 20 g to 600 g a.i./ha. When the compounds are used as seed dressings, dosages of from 10 mg to 1 g of active ingredient per kg of seed are advantageously employed.
The agrochemical compositions generally comprise 0.1 to 99 % by weight, preferably 0.1 to 95 % by weight, of a compound of formula I, 99.9 to 1 % by weight, preferably 99.8 to 5 % by weight, of a solid or liquid adjuvant and 0 to 25 % by weight, preferably 0.1 to 25 % by weight, of a surfactant.
Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ dilute formulations.

The compositions may also comprise further auxiliaries, such as stabilisers, antifoams, viscosity regulators, binders or tackifiers, as well as fertilisers or other active ingredients for obtaining special effects.
The compounds of formula I can be mixed with other fungicides, producing in some cases unexpected synergistic effects.
Especially preferred mixing partners are
azoles, as azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, imibenconazole, ipconazole, metconazole, myclobutanil, pefurazoate, penconazole, pyrifenox, prochloraz, propiconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, triticonazole;

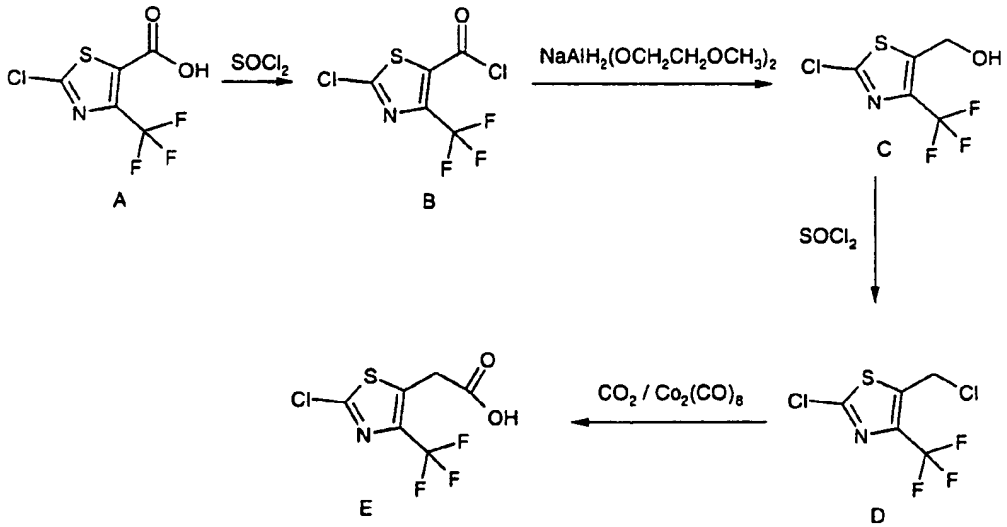
pyrimidinyl carbinoles, as ancymidol, fenarimol, nuarimol;
2-amino-pyrimidines, as bupirimate, dimethirimol, ethirimol;
morpholines, as dodemorph, fenpropidin, fenpropimorph, spiroxamin, tridemorph;
anilinopyrimidines, as cyprodinil, mepanipyrim, pyrimethanil;
pyrroles, as fenpiclonil, fludioxonil;
phenylamides, as benalaxyl, furalaxyl, metalaxyl, R-metalaxyl, ofurace, oxadixyl;
benzimidazoles, as benomyl, carbendazim, debacarb, fuberidazole, thiabendazole;
dicarboximides, as chlozolinate, dichlozoline, iprodione, myclozoline, procymidone, vinclozolin;
carboxamides, as carboxin, fenfuram, flutolanil, mepronil, oxycarboxin, thifluzamide;
guanidines, as guazatine, dodine, iminoctadine;
strobilurines, as azoxystrobin, kresoxim-methyl, SSF-126 (metominostrobin or fenominostrobin; SSF-129 (α-methoximino-N-methyl-2-[(2,5-dimethylphenoxy)methyl]-benzeneacetamide), trifloxystrobin (2-[α-{[(α-methyl-3-trifluormethyl-benzyl)imino]-oxy}-o-tolyl] -glyoxylsäure-methylester-O-methyloxim);
dithiocarbamates, as ferbam, mancozeb, maneb, metiram, propineb, thiram, zineb, ziram;
N-halomethylthiodicarboximides, as captafol, captan, dichlofluanid, fluoromide, folpet, tolyfluanid;
copper compounds, as bordeaux-mixture, copper hydroxide, copper oxychloride, copper sulfate, cuprous oxide, mancopper, oxine-copper;
nitrophenol-derivatives, as dinocap, nitrothal-isopropyl;
organo-P-derivatives, as edifenphos, iprobenphos, isoprothiolane, phosdiphen, pyrazophos, tolclofos-methyl;
other compounds, as acibenzolar-S-methyl, anilazine, blasticidin-S, chinomethionat, chloroneb, chlorothalonil, cymoxanil, dichlone, diclomezine, dicloran, diethofencarb, dimethomorph, dithianon, etridiazole, famoxadone, fentin, ferimzone,fluazinam, flusulfamide, fenhexamid, fosetyl-aluminium, hymexazol, kasugamycin, methasulfocarb, pencycuron, phthalide, polyoxins, probenazole, propamocarb, pyroquilon, quinoxyfen, quintozene, sulfur, triazoxide, tricyclazole, triforine, validamycin.

Examples

A. Preparation Examples

Abbreviations: Me = methyl; Et = ethyl; Pr = n-propyl; i-Pr = isopropyl; Bu = n-butyl; i-Bu = isobutyl; sec-Bu = sec-butyl; t-butyl = tert-butyl, Ph = phenyl; Ac = acetyl, THF = tetrahydrofuran; TPP = triphenylphosphine; Val = valine; m.p. = melting point

1. Compound No.1.1 (E)



A mixture of thiazole A (synthesized according to EP 0279239) (25.5 g, 0.11 Mol) and thionyl chloride (26.2 g, 0.22 Mol) in 25ml of toluene, is held at reflux for 1.5 hours. After, evaporation of the toluene under reduced pressure, 24 g of the acid chloride B (b.p 90-92°, 45mbar) is distilled through a Vigreux column.

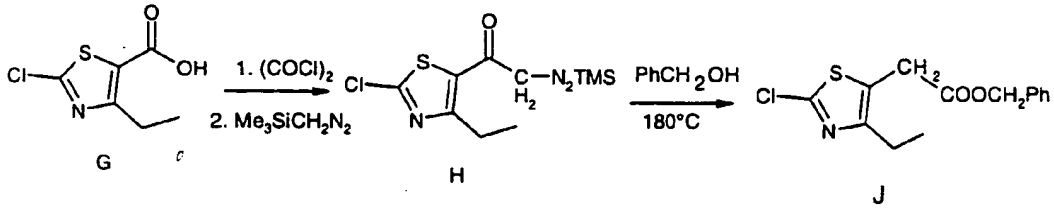
To the acid chloride B (97.5 g, 0.39 Mol) in 1l dry tetrahydrofuran at -70°C under nitrogen atmosphere, $NaAlH_2(OCH_2CH_2OCH_3)_2$ (commercial solution 3.5M in toluene, 0.429Mol), diluted in 300ml of toluene, is added dropwise. After 45min of stirring at -70°C, the cooling bath is removed and the reaction is quenched with 370 ml of 3.5N HCl is added. The organic phase extracted with ethyl acetate, dried over sodium sulfate, concentrated under reduced pressure and flash-chromatographed to afford 67.5g of the alcohol C as an oil.

A mixture of alcohol C (60 g, 0.276 Mol) and thionyl chloride (98.5 g, 0828 Mol) in 400 ml of dichloromethane containing 0.1 ml of dimethyl formamide is stirred at reflux for 8 hours: Another portion of thionyl chloride (16.4 g, 0.138 Mol) is then added and the reaction

heated for additional 16 hours. After the reaction is cooled down to room temperature, the solvent is removed under reduced pressure (60°C, 200 mbar) and the resulting crude yellow oil is distilled through a 5 cm Vigreux column (92-95°C, 20 mbar) to give 53.5 g of compound D as an colorless oil.

A mixture of compound D (125 g, 1.059 Mol), benzyltriethylammonium chloride (4.8 g, 0.042 Mol), cobalt carbonyl (7.2 g, 0.042 Mol), sodium carbonate (101 g, 2.4 Mol), 1.5 l of water and 1.36l of dichloromethane is stirred under carbon monoxide pressure (10 bars) for 24 hours at room temperature. The biphasic mixture is then filtered over celite, extracted two times with dichloromethane. The water phase is acidified with105 ml of concentrated HCl and extracted with ethyl acetate. The organic layer is then washed with brine, dried over sodium sulfate, treated with active charcoal at 60°C, filtered over celite and concentrated in vacuo to give 114 g of the acid E which is used without further purification.

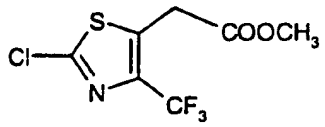
2. Compound No 2.5 (J) (by Arndt-Eistert-reaction)



G H J

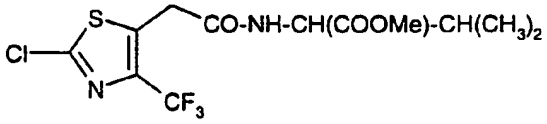
To compound G (2.0 g, 10.44 mmol) dissolved in 20 ml of dichloromethane at 0°C, is added oxalyl chloride (0.9 ml, 10.5 mmol). After the development of carbon dioxide stopped, 0.1 ml of dimethylformamide is added and the yellow suspension is stirred at room temperature for 3 hours. The resulting yellow solution is then concentrated under reduced pressure, dissolved in a mixture of 10 ml tetrahydrofuran and 10 ml acetonitrile, cooled down to 0°C, and successively treated with triethylamine (1.8 ml), trimethylsilyldiazomethane (commercial 2N solution in hexane) (6.05 ml, 13.05 mmol). After 12 hours of stirring at 0°C, the solvents are evaporated under reduced pressure, and the intermediate diazoketone G is rearanged in a mixture of 13 ml of benzylalcohol and 13 ml of trimethylpyridine at 180°C for 8 min. The dark mixture is cooled down to room tempature, diluted with ethyl acetate, washed 3 times with citric acid (10% aqueous solution). The ethyl acetate layer is dried over magnesium sulfate, filtered, evaporated under reduced pressure, and flash-chromatographed to give the compound J as an oil.

3. Compound No.1.2



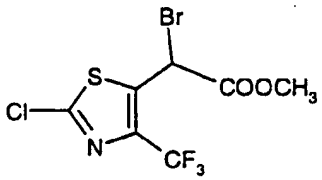
2-Chloro-4-trifluoromethyl-5-acetic acid (10 g, 40.71 mmol) in 100 ml of methanol is heat-refluxed in presence of concentrated sulfuric acid (4 g, 40.71 mol) for 12hours. After cooling at room temperature, the methanol is distilled off under reduced pressure, the residue is dissolved in ethyl acetate, and successively washed with a saturated solution of sodium bicarbonate (3 times) and brine. After drying over magnesium sulfate, the ethyl acetate layer is filtered, evaporated under reduced pressure and flash-chromatographed on silica-gel to give 10.36g of the the title compound as a pale red oil.

4. Compound No.1.21



The acid chloride of comp. 1.2 (78.5 g, 0.2973 Mol) and L-Valine methyl ester hydrochloride are suspended in 600 ml of toluene, and heated at 110°C for 25 minutes. The resulting clear solution is cooled down to room temperature, extracted successively with water, a saturated solution of sodium bicarbonate, brine. The organic layer is then dried over sodium sulfate and the solvent removed under reduced pressure to give a crude oil which is chromatographed on silica-gel to afford 102g of the title compound (mp:51-53°C).

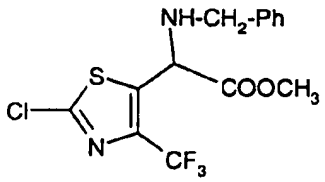
5. Compound No.1.76



A mixture of compound 1.2 (9 g, 34.7 mmol) and N-Bromosuccinimide (15.49 g, 87 mmol) in 200 ml of carbon tetrachloride, irradiated with a 150W quartz lamp is heated at reflux temperature. After 1.5 hours of stirring, the mixture is cooled down to room temperature and

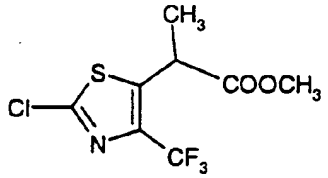
filtered over celite. After removal of the solvent under reduced pressure, the filtrate is suspended in hexane at 60°C and the solid filtered over celite. The hexane evaporated under reduced pressure to give a red oil, which after distillation (150°C, 0.13mbars) gives 10g of the title compound as a pale red oil.

6. Compound No. 1.97



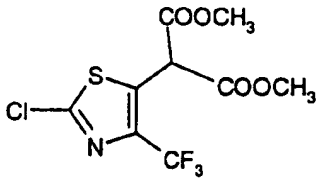
A mixture of compound 1.76 (1 g, 2.9 mmol) and (0.63 g, 5.9 mmol) of benzylamin is stirred at room temperature for 4 hours. After completion of the reaction, the reaction mixture is removed under reduced pressure, and chromatographed on silica to give 0.8 g of the title compound as an oil.

7. Compound No.1.82



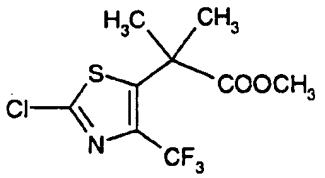
Compound 1.2 (1 g, 3.8 mmol) is added to a suspension of sodium hydride (55% in mineral oil) (0.17g, 4,2mmol) in tetrahydrofuran at -50°C, and the resulting red solution stirred for 1hour at -35°C. After this period, methyl iodide (0.7 g, 5 mmol) is rapidly added. After 2 hours of stirring, the reaction is quenched with a saturated aqueous ammonium chloride solution, and extracted with ethyl acetate. The organic layer is dried over magnesium sulfate, evaporated under reduced pressure and chromatographed on silica to give 0.72 g of the title compound as a pale yellow oil.

8. Compound No.1.92



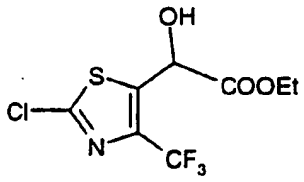
Compound 1.2 (1 g, 3.8 mmol) is added to a suspension of sodium hydride (55% in mineral oil) (0.17 g, 4,2 mmol) in dry tetrahydrofuran at -50°C, and the resulting red solution stirred for 1hr at -35°C. Methyl chloroformiate (6 mmol) is then added, and after 2hours of stirring, the reaction is quenched with a saturated aqueous ammonium chloride solution, and heated up to room temperature. After extraction with ethyl acetate, the organic layer is dried over magnesium sulfate, filtered and evaporated under reduced pressure. The reaction mixture is purified on silica to afford 0.79g of the title compound as a white solid.

9. Compound No. 1.99



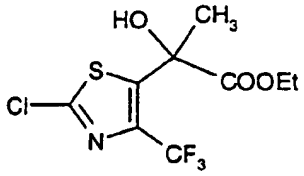
To a suspension of sodium hydride (55% in mineral oil)(0.61 g, 25.4 mmol) at -50°C, is added compound 1.2 (3 g, 11.55 mmol). After 2.5 hours of stirring at -30°C, the red mixture is cooled down to -78°C, treated with methyliodide (4.92 g, 34,65 mmol), and slowly heated up to -20C over a period of 1.5hrs. After hydrolysis with a saturated aqueous ammonium chloride solution, the reaction mixture is extracted with ethyl acetate, dried over magnesium sulfate, and after evaporation of the solvent under reduced pressure, the resulting crude material is purified by flash-chromatography to give 2.06g of the title compound as an oil.

10. Compound No.1.100



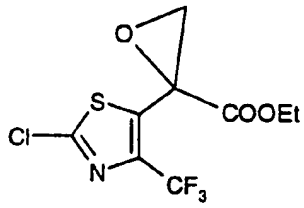
To a tetrahydrofuran solution kept at -78°C of lithium diisopropylamide, prepared at 0°C from diisopropylamine (0.83 ml, 5.9 mmol) and n-butyl lithium (3.33 ml, 5.3 mmol), 2-chloro-4-trifluoromethyl-thiazole is slowly added (1 g, 5.33 mmol). After 2 hours of stirring, the green solution is transferred, via a canula to a flask containing a solution of ethylglyoxylate (50% toluene commercial solution) (15ml, 10.6mmol) in tetrahydrofuran kept at -78°C. After 5 minutes, the mixture is treated with a saturated aqueous ammonium chloride solution, extracted with ethyl acetate and concentrated in vacuo. The resulting crude residue is then purified by chromatography on silica-gel to give 0.28 g of the title compound as an oil.

11. Compound No.1.106



2-chloro-4-trifluoromethyl-thiazole (0.5 g, 2,66 mmol) dissolved in tetrahydrofurane is treated at -78°C with lithium hexamethyldisilyamide (commercial solution, 1M in tetrahydrofuran, 2,67ml), stirred for 1.5 hours, followed by the addition of ethylpyruvate (0.305 ml, 2.9 mmol). After the reaction is completed, it is quenched with a saturated aqueous ammonium chloride solution, extracted with ethyl acetate. The organic layer is dried over magnesium sulfate, concentrated under reduced pressure and chromatographed on silica-gel to afford 0.730 g of the title compound as a yellow oil.

12. Compound No. 1.113



2-Chloro-4-trifluoromethyl-thiazole (2 g, 10.66 mmol) dissolved in tetrahydrofuran is treated at -78°C with lithium hexamethyldisilyamide (commercial solution, 1M in tetrahydrofuran, 2,67 ml), stirred for 1.5 hours, followed by the addition of ethylbromopyruvate (1.79 ml, 12.79 mmol). After the reaction is completed, it is quenched with a saturated aqueous ammonium chloride solution and heated up to room temperature. The reaction mixture is then extracted with ethyl acetate, the organic layer dried over magnesium sulfate, the solvent removed under reduced pressure, and the crude material chromatographed on silica-gel to afford 0.254g of 2.08g of the title compound as oils.

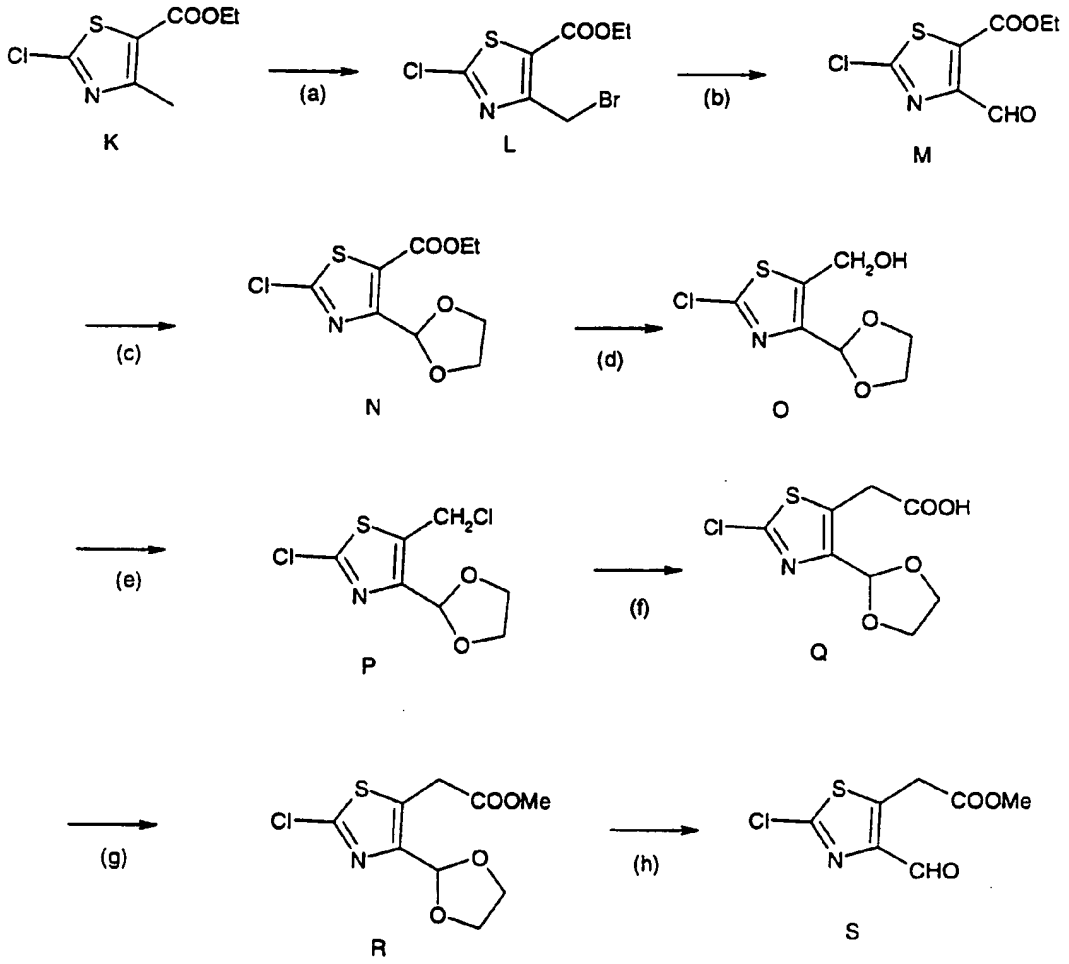
13. Compounds Nos. 2.18 (Q), 2.19 (R), 2.25 (S) (Scheme 13)

(a) A mixture of compound K (179 g, 0.871 Mol) NBS (159.8 g, 0.871 Mol) and Azoisobutyronitrile (AIBN) (14.6 g, 87 mmol) in 600 ml of CCl4 is heated at reflux for 16 hrs. After cooling, the crude mixture is filtered, concentrated under reduced pressure and flash-chromatographed to afford 190 g of compound L contaminated with the starting material K.

(b) To a solution of compound L (189.4 g, 0.666 Mol) in 1.5 l of acetonitrile, is added 0.3 l of 4A molecular sieves followed by N-methylmorpholine-N-oxide (139.2 g, 0.99 Mol). After 2.5 hrs. of stirring at room temperature, the mixture is filtered on silicagel, concentrated in vacuo and purified by flash-chromatography to give 92 g of aldehyde M.

(c) A solution of aldehyde L (91.25 g, 0.415 Mol), ethylene glycol (29 ml, 0.5 Mol) and p-toluenesulfonic acid (9.12 g, 41 mmol) is heated for 16 hrs. at reflux in 300 ml of benzene while water is destilled off. After cooling, the crude mixture is extracted with water and ether, the organic phase is then dried over $MgSO_4$, concentrated under reduced pressure and purified by flash-chromatography to give 65 g of the dioxolane N.

Scheme 13



(d) To a suspension of $LiAlH_4$ (1.78 g, 45.4 mmol) in 220 ml of dry THF at 0°C, is added dropwise compound N (10 g, 37.9 mmol) dissolved in 100 ml of THF. After 5 min of stirring the reaction is completed. The mixture is successively treated with 1.78 ml of water, 1.78 ml of NaOH (15% aqueous solution) and 5.34 ml of water. The suspension is then filtered over celite, extracted 3 times with ethylacetate and water. The combined organic phases are concentrated under reduced pressure and chromatographed on silica to afford 31 g of the alcohol O.

(e) To a solution of compound O (9.85 g, 44.46 mmol) in 180 ml of CCl_4 is added triphenlyphosphine (11.8 g, 44.46 mmol). The mixture is stirred at 85°C for 24 hrs. After cooling, the crude solution is concentrated under reduced pressure and purified by chromatography on silica to afford 6.4 g of compound P.

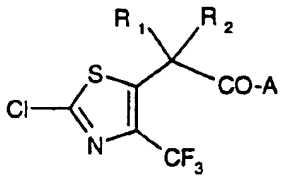
(f) A mixture of compound P (7.43 g, 30.9 mmol), benzyltriethylammonium chloride (283 mg, 1.24 mmol), cobalt carbonyl (423 mg, 1.24 mmol), sodium carbonate (5.83 g, 69.4 mmol), 68 ml of water and 62 ml of dichloromethane is stirred under carbon monoxide pressure (10 bars) for 24 hours at room temperature. The biphasic mixture is then filtered over celite, extracted two times with dichloromethane. The water phase is acidified to pH 2 with concentrated HCl and extracted with ethyl acetate. The organic layer is then washed with brine, dried over sodium sulfate, filtered and concentrated in vacuo to give 3.2 g of the acid Q which is used without further purification.

(g) A solution of the acid Q in THF is carefully treated at room temperature with an ether solution diazomethane. The reaction is monitored by tlc. After completion of the reaction, the crude mixture is concentrated under reduced pressure and chromatographed to 2 g of the methylester R.

(h) Compound R (1.61 g, 6.47 mmol) is stirred for 40 min in 19 ml of THF, 19 ml of water and 9 ml of trifluoroacetic acid. After evaporation of the solvent, the crude mixture is diluted with ether and washed with $NaHCO_3$ (sat. aqueous solution). The ether phase is concentrated under reduced pressure to afford the aldehyde S which is an oil.
The aldehyde group may be converted by known methods into many different other groups.

Table 1.A

Table1



No.	R_1	R_2	A	Phys. data m.p °C
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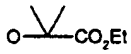
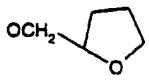
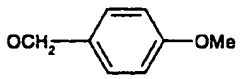
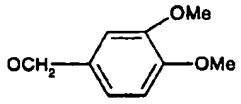
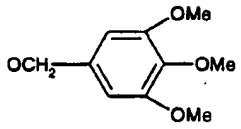
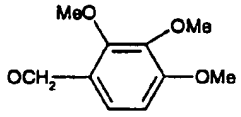
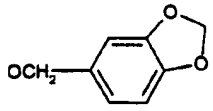
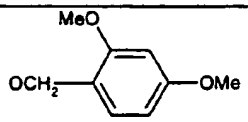
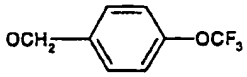
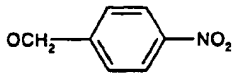
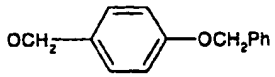
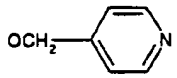
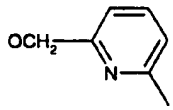
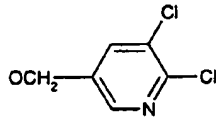
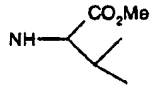
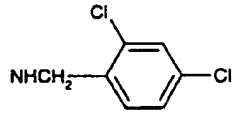
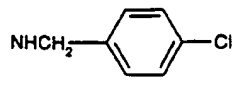
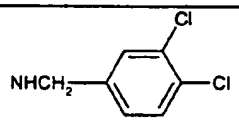
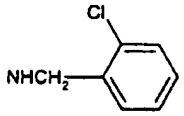
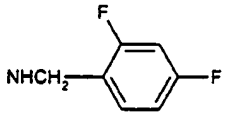
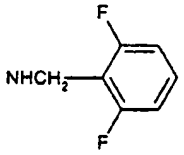
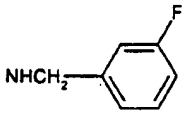
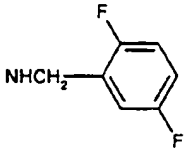
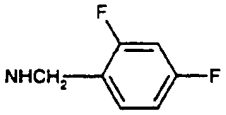
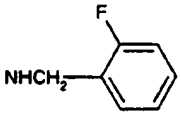
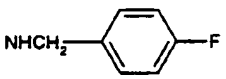
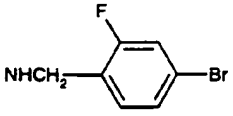
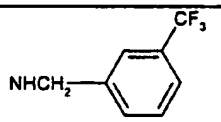
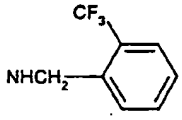
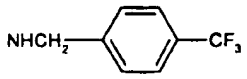
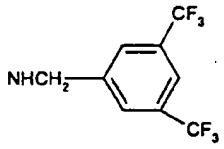
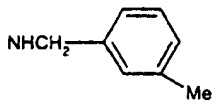
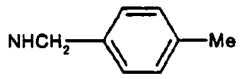
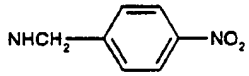
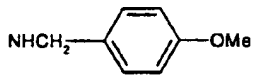
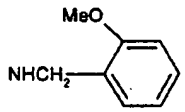
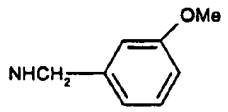
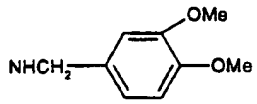
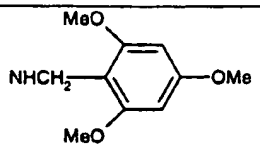
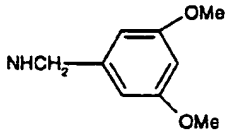
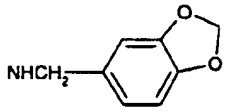
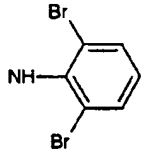
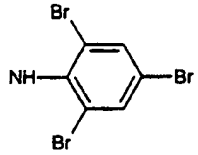
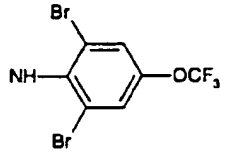
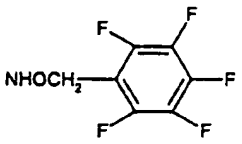
1.2.	H	H	OMe	oil
1.3.	H	H		oil
1.4.	H	H	O*t*-Bu	oil
1.5.	H	H	$OCH_2CH=CH_2$	oil
1.6.	H	H		oil
1.7.	H	H	OCH_2Ph	oil
1.8.	H	H		oil
1.9.	H	H		solid
1.10.	H	H		oil
1.11.	H	H		oil
1.12.	H	H		oil

No.	R_1	R_2	A	Phys. data m.p °C
1.13.	H	H		solid
1.14.	H	H		oil
1.15.	H	H		solid
1.16.	H	H		oil
1.17.	H	H		oil
1.18.	H	H		90-91
1.19.	H	H		oil
1.20.	H	H	OCH_2COMe	oil
1.21.	H	H		51-53
1.22.	H	H	NMe_2	
1.23.	H	H	NHMe	
1.24.	H	H	NHEt	
1.25.	H	H	NHn-Bu	
1.26.	H	H	NHt-Bu	
1.27.	H	H		127-8
1.28.	H	H		142-3

No.	R_1	R_2	A	Phys. data m.p °C
1.29.	H	H		122-3
1.30.	H	H		solid
1.31.	H	H		105-6
1.32.	H	H		51-2
1.33.	H	H		solid
1.34.	H	H		85-6
1.35.	H	H		solid
1.36.	H	H		115-6
1.37.	H	H		110-20
1.38.	H	H		123-4

No.	R_1	R_2	A	Phys. data m.p °C
1.39.	H	H		98
1.40.	H	H		97-101
1.41.	H	H		102-4
1.42.	H	H		106-7
1.43.	H	H		99-101
1.44.	H	H		120
1.45.	H	H		solid
1.46.	H	H	$NHCH_2Ph$	110-1
1.47.	H	H		126-30
1.48.	H	H		115
1.49.	H	H		107-8
1.50.	H	H		132-3

No.	R_1	R_2	A	Phys. data m.p °C
1.51.	H	H		159-60
1.52.	H	H		140-2
1.53.	H	H		130-1
1.54.	H	H		188-9
1.55.	H	H		solid
1.56.		H		51
1.57.	H	H	$ONHCOOCH_2Ph$	oil
1.58.	H	H	$ONHCH(CH_3)_2$	oil
1.59.	H	H	$ONHC(CH_3)_3$	oil
1.60.	H	H	$ON=C(CH_3)OEt$	oil
1.61.	H	H	$ONHCOOC(CH_3)_3$	oil
1.62.	H	H	ONHCOOEt	oil
1.63.	H	H	$ONHSO_2Ph$	114-20
1.64.	H	H	$NHOC(Ph)_3$	177
1.65.	H	H	$NHOCH_2Ph$	78-85
1.66.	H	H	NHOMe	117-8
1.67.	H	H	$NHOCH_2CH=CH_2$	73-4

No.	R_1	R_2	A	Phys. data m.p °C
1.68.	H	H	$NHOC(CH_3)_3$	solid
1.69.	H	H	NHOPh	
1.70.	H	H		solid
1.71.	H	H	SMe	oil
1.72.	H	H	SEt	
1.73.	H	H	SPh	
1.74.	H	H	SCH_2Ph	
1.75.	Br	H	OH	oil
1.76.	Br	H	OMe	oil
1.77.	F	H	OH	
1.78.	F	H	OMe	oil
1.79.	Cl	H	OMe	
1.80.	Cl	H	OH	
1.81.	Me	H	OH	oil
1.82.	Me	H	OMe	oil
1.83.	Et	H	OMe	oil
1.84.	Et	H	OH	oil
1.85.	Pr	H	OH	
1.86.	Pr	H	OMe	
1.87.	nBu	H	OH	
1.88.	nBu	H	OMe	
1.89.	$CH_2CH=CH_2$	H	OH	oil
1.90.	CH_2Ph	H	OH	127-8°C
1.91.	CH_2Ph	H	OMe	oil
1.92.	COOMe	H	OMe	oil
1.93.	CH_2COOH	H	OH	130-1°C
1.94.	NH_2	H	OH	166-7°C
1.95.	$NH_2.HCl$	H	OMe	176-7°C
1.96.	NEt_2	H	OMe	56-8°C

No.	R_1	R_2	A	Phys. data m.p °C
1.97.	$NHCH_2Ph$	H	OMe	oil
1.98.	Me	Me	OH	137-8°C
1.99.	Me	Me	OMe	oil
1.100.	OH	H	OEt	oil
1.101.	OH	H	OH	
1.102.	OAc	H	OEt	oil

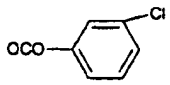
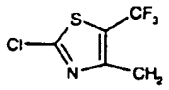
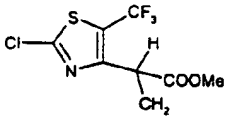
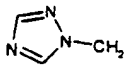
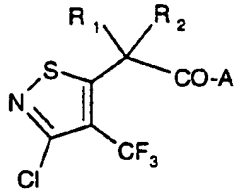
	R_1	R_2	A	
1.103.		H	OEt	oil
1.104.	OMe	H	OEt	oil
1.105.	$OSi\text{-}t\text{-}BuMe_2$	H	OEt	oil
1.106.	OH	Me	OEt	oil
1.107.	OH	CF_3	OMe	oil
1.108.	OH	Ph	OEt	77-9°C
1.109.	OH	CH_2Br	OEt	oil
1.110.		OH	OEt	oil
1.111.		H	OMe	151-2°C
1.112.	R1+R_2 =O	H	OEt	oil
1.113.	R1+R_2 	H	OEt	oil
1.114.		OH	OEt	oil

Table 1.B

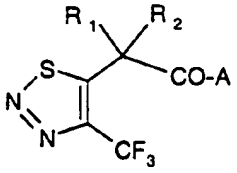
Compounds of the formula



wherein the R_1, R_2 and A have the meanings of the corresponding compounds of Table 1.A.

Table 1.C

Compounds of the formula

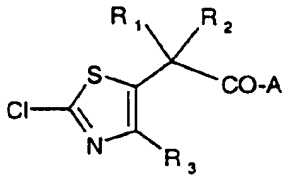


wherein R_1, R_2 and A have the meanings of the corresponding compounds of Table 1.A.

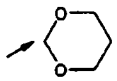
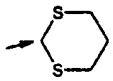
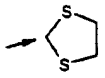
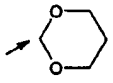
Phys. data of compound(s) of Table 1.C:

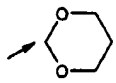
No.	R_1	R_2	A	Phys. data m.p. °C
1.C.1	H	H	OH	oil

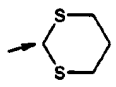
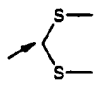
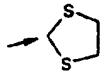
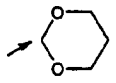
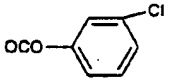
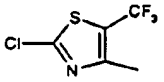
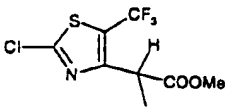
Table 2.A



No	R_1	R_2	R_3	A	Phys.data m.p.°C
2.1.	H	H	H	OCH_2Ph	oil
2.2.	H	H	H	OH	
2.3.	H	H	Me	OCH_2Ph	oil
2.4.	H	H	Me	OH	
2.5.	H	H	Et	OCH_2Ph	oil
2.6.	H	H	Et	OMe	oil
2.7.	H	H	Et	OH	191-3
2.8.	H	H	n-Pr	OMe	oil
2.9.	H	H	2-Pr	OMe	oil
2.10.	H	H	2-Pr	OH	
2.11.	H	H	cyclo-Pr	OMe	oil
2.12.	H	H	t-Bu	OMe	oil
2.13.	H	H	t-Bu	OH	
2.14.	H	H	Ph	OMe	oil
2.15.	H	H	CH_2Ph	OMe	oil
2.16.	H	H	2-thiophenyl	OMe	oil
2.17.	H	H	COOMe	OMe	oil
2.18.	H	H		OH	oil
2.19.	H	H		OMe	oil

No	R_1	R_2	R_3	A	Phys.data m.p.°C
2.20.	H	H		OH	
2.21.	H	H		OH	
2.22.	H	H		OH	
2.23.	H	H		OH	
2.24.	H	H		OMe	
2.25.	H	H	CHO	OMe	oil
2.26.	H	H	CH_2OH	OMe	solid
2.27.	H	H	CH_2Cl	OMe	oil
2.28.	H	H	CH_2Br	OMe	
2.29.	H	H	CH_2F	OMe	
2.30.	H	H	CH_2NHCOO-t-Bu	OMe	
2.31.	H	H	CH_2NEt_2	OMe	
2.32.	H	H	CH_2NH_2	OMe	
2.33.	H	H	CH_2NHOH	OMe	
2.34.	H	H	$CH=CH_2$	OMe	
2.35.	H	H	CH=CHCOOMe	OMe	
2.36.	H	H	CH=CHMe	OMe	
2.37.	H	H	$CH=CBr_2$	OMe	
2.38.	H	H	CHOHMe	OMe	
2.39.	H	H	CHOHEt	OMe	
2.40.	H	H	CHOHClMe	OMe	
2.41.	H	H	CHOHFMe	OMe	
2.42.	H	H	CHOHBrMe	OMe	

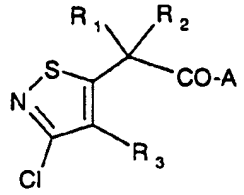
No	R_1	R_2	R_3	A	Phys.data m.p.°C
2.43.	H	H	$CH=CF_2$	OMe	
2.44.	H	H	COEt	OMe	
2.45.	H	H	CHOHMe	OMe	
2.46.	H	H	CHClMe	OMe	
2.47.	H	H	CHFMe	OMe	
2.48.	H	H	CHBrMe	OMe	
2.49.	H	H	4-Cl-Ph	OMe	
2.50.	H	H	3-MeO-Ph	OMe	
2.51.	H	H	2,4-Me_2-Ph	OMe	
2.52.	H	H		OMe	
2.53.	Br	H	$COHMe_2$	OCH_2Ph	
2.54.	Br	H	$COHEt_2$	OH	
2.55.	F	H	Et	OCH_2Ph	
2.56.	Cl	H	Et	OH	
2.57.	Cl	H	n-Pr	OCH_2Ph	
2.58.	Me	H	2-Pr	OMe	
2.59.	Et	H	cyclo-Pr	OH	
2.60.	Et	H	t-Bu	OMe	
2.61.	Pr	H	t-Bu	OMe	
2.62.	Pr	H	Ph	OH	
2.63.	nBu	H	CH_2Ph	OMe	
2.64.	nBu	H	2-thiophen	OMe	
2.65.	$CH_2CH=CH_2$	H	COOMe	OH	
2.66.	CH_2Ph	H		OMe	
2.67.	CH_2Ph	H		OMe	
2.68.	COOMe	H		OMe	

No	R_1	R_2	R_3	A	Phys.data m.p.°C
2.69.	CH_2COOH	H		OMe	
2.70.	NH_2	H		OMe	
2.71.	$NH_2.HCl$	H		OCH_2Ph	
2.72.	NEt_2	H		OH	
2.73.	$NHCH_2Ph$	H	CHO	OCH_2Ph	
2.74.	Me	H	CH_2OH	OH	
2.75.	Me	H	CH_2Cl	OCH_2Ph	
2.76.	OH	H	CH_2Br	OMe	
2.77.	OH	H	CH_2F	OH	
2.78.	OAc	H	$CHCl_2$	OMe	
2.79.		H	H	OMe	
2.80.	OMe	H	Me	OH	
2.81.	$OSi\text{-}t\text{-}BuMe_2$	H	Me	OMe	
2.82.	OH	H	Et	OMe	
2.83.	OH	H	Et	OH	
2.84.	OH	H	Et	OMe	
2.85.	OH	H	n-Pr	OMe	
2.86.		CF_3	2-Pr	OMe	
2.87.		Ph	2-Pr	OMe	
2.88.	R_1+R_2 =O	CH_2Br	cyclo-Pr	OMe	

No	R_1	R_2	R_3	A	Phys.data m.p.°C
2.89.	R_1+R_2 	OH	t-Bu	OMe	
2.90.	H	H	cyclo-Pr	OCH_2Ph	oil

Table 2.B

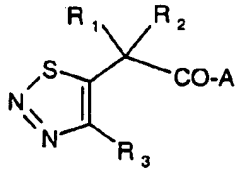
Compounds of the formula



wherein R_1, R_2, R_3 and A have the meanings of the corresponding compounds of Table 2.A.

Table 2.C

Compounds of the formula



wherein R_1, R_2, R_3 and A have the meanings of the corresponding compounds of Table 2.A.

Phys. data of compounds of Table 2.C:

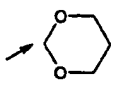
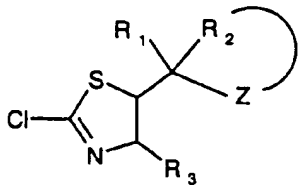
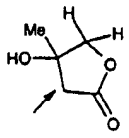
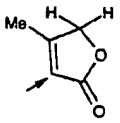
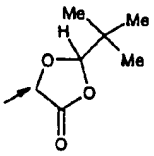
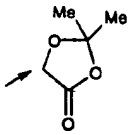
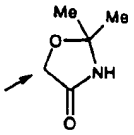
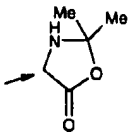
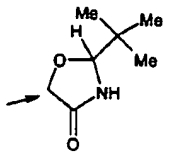
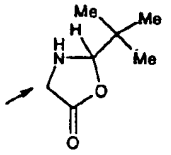
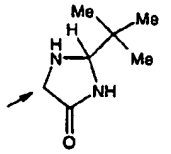
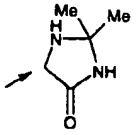
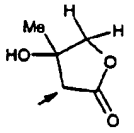
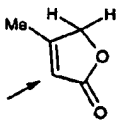
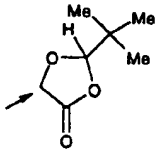
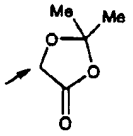
No.	R_1	R_2	R_3	A	Phys.data m.p.°C
2.C.3	H	H	Me	OCH_2Ph	oil
2.C.5	H	H	Et	OCH_2Ph	oil
2.C.7	H	H	Et	OH	oil
2.C.20	H	H		OH	solid
2.C.90	H	H	cyclo-Pr	OCH_2Ph	oil

Table 3.A



No.	R_1	R_2+ Z	R_3	Phys. data m.p.°C
3.1.	H		CF_3	159-61°C
3.2.		R_1+R_2+Z 	CF_3	oil
3.3.	H		CF_3	solid
3.4.	H		CF_3	solid
3.5.	H		CF_3	
3.6.	H		CF_3	

No.	R_1	R_2+ Z	R_3	Phys. data m.p.°C
3.7.	H		CF_3	
3.8.	H		CF_3	
3.9.	H		CF_3	
3.10.	H		CF_3	
3.11.	H		Me	
3.12.	H	R1+R2+Z 	Me	
3.13.	H		Et	
3.14.	H		Et	

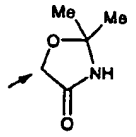
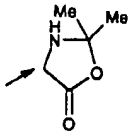
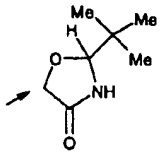
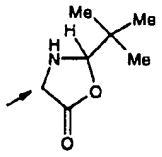
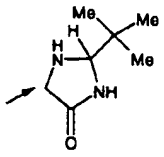
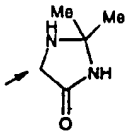
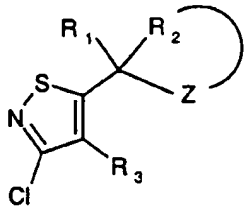
No.	R_1	R_2+ Z	R_3	Phys. data m.p.°C
3.15.	H		Et	
3.16.	H		n-Pr	
3.17.	H		2-Pr	
3.18.	H		2-Pr	
3.19.	H		cyclo-Pr	
3.20.	H		t-Bu	

Table 3.B

Compounds of the formula

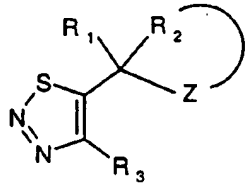


I

wherein R_1, R_2, R_3 and Z have the meanings of the corresponding compounds of Table 3.A.

Table 3.C

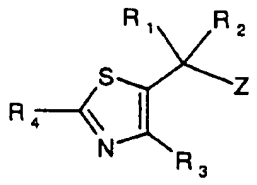
Compounds of the formula



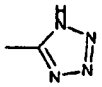
I

wherein R_1, R_2, R_3 and Z have the meanings of the corresponding compounds of Table 3.A.

Table 4.A



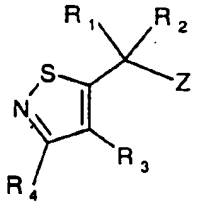
No.	R_1	R_2	R_3	R_4	Z	Phys.data m.p.°C
4.1.	H	H	CF_3	Ph	COOMe	oil
4.2.	H	H	Me	CF_3	COOH	
4.3.	H	H	CF_3	H	COOH	
4.4.	H	H	CF_3	H	COOMe	oil
4.5.	H	H	Me	H	COOEt	solid
4.6.	R_1+R_2 =O		Me	H	COOEt	solid
4.7.	R_1+R_2 =O		Me	NHCOOEt	COOEt	solid
4.8.	R_1+R_2 =O		Me	NHn-Bu	COOEt	solid
4.9.	R_1+R_2 =O		Me	NHt-Bu	COOEt	solid
4.10.	H	H	Me	NHMe	COOEt	solid
4.11.	H	H	Me	$NHCH_2CH=CH_2$	COOH	solid
4.12.	H	H	Et	NH-t-Bu	COOEt	solid
4.13.	H	H	Ph	p-$PhSO_2NH_2$	COOEt	solid
4.14.	H	H	p-ClPh	NHPh	COOEt	solid
4.15.	H	H	OH	OH	COOH	solid
4.16.	R_1+R_2 =O		Me	NH-COOEt	COSMe	
4.17.	R_1+R_2 =O		Me	NH-n-Bu	COSMe	
4.18.	R_1+R_2 =O		Me	NH-t-Bu	COSMe	
4.19.	H	H	CF_3	CF_3	COSMe	
4.20.	H	H	CF_3	OMe	COOMe	
4.21.	H	H	CF_3	OEt	COOMe	
4.22.	H	H	CF_3	O-n-Pr	COOMe	
4.23.	H	H	CF_3	SMe	COOMe	
4.24.	H	H	CF_3	SEt	COOMe	

No.	R_1	R_2	R_3	R_4	Z	Phys.data m.p.°C
4.25.	H	H	CF_3	SPh	COOMe	
4.26.	H	H	CF_3	NMe_2	COOMe	
4.27.	H	H	CF_3	NEt_2	COOMe	
4.28.	H	H	CF_3	NH_2	COOMe	
4.29.	H	H	CF_3	SH	COOMe	
4.30.	H	H	CF_3	NH_2	CSOMe	
4.31.	H	H	Me	Cl		solid
4.32.	H	H	CF_3	Ph	CSOMe	
4.33.	H	H	Me	CF_3	CSOH	
4.34.	H	H	CF_3	H	CSOH	
4.35.	H	H	CF_3	H	CSOMe	
4.36.	H	H	Me	H	CSOEt	
4.37.	R_1+R_2 =S		Me	H	COOEt	
4.38.	R_1+R_2 =S		Me	NHCOOEt	COOEt	
4.39.	R_1+R_2 =S		Me	NH-n-Bu	CSOEt	
4.40.	R_1+R_2 =S		Me	NH-t-Bu	CSOEt	
4.41.	H	H	Me	NHMe	CSOEt	
4.42.	H	H	Me	$NHCH_2CH=CH_2$	CSOH	
4.43.	H	H	Et	NHt-Bu	CSOEt	
4.44.	H	H	Ph	p-$PhSO_2NH_2$	CSOEt	
4.45.	H	H	p-ClPh	NHPh	CSOEt	
4.46.	H	H	OH	OH	CSOH	
4.47.	R_1+R_2 =O		Me	NH-COOEt	CSSMe	
4.48.	R_1+R_2 =O		Me	NHn-Bu	CSSMe	
4.49.	R_1+R_2 =S		Me	NHt-Bu	CSSMe	
4.50.	H	H	Et	CF_3	COSMe	
4.51.	H	H	Et	OMe	COOMe	
4.52.	H	H	n-Pr	OEt	COOMe	
4.53.	H	H	i-Pr	n-Pr	COOMe	
4.54.	H	H	OH	SMe	COOMe	

No.	R_1	R_2	R_3	R_4	Z	Phys.data m.p.°C
4.55.	H	H	OH	SEt	COOMe	
4.56.	H	H	CF_3	SPh	CONHMe	
4.57.	H	H	CF_3	NMe_2	CONHMe	
4.58.	H	H	CF_3	NEt_2	CONHMe	
4.59.	H	H	CF_3	NH_2	CSNHMe	
4.60.	H	H	CF_3	SH	CSNHMe	
4.61.	H	H	CF_3		CSNHMe	

Table 4.B

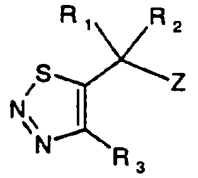
Compounds of the formula



wherein R_1, R_2, R_3, R_4 and Z have the meanings of the corresponding compounds of Table 4.A.

Table 4.C

Compounds of the formula



wherein R_1, R_2, R_3 and Z have the meanings of the corresponding compounds of Table 4.A.

Formulation Examples

for similar purposes of pesticidal use are descibed for example in WO 97/33890.

Biological Examples

Example B.1: Immunization of Cucumis sativus L. against Colletotrichum lagenarium

a) After a cultivation period of 2 weeks, cucumber plants are sprayed with a spray mixture prepared from a wettable powder formulation of the test compound (concentration: 200 ppm). After 72 hours, the plants are infected with a spore suspension (1.0×10^5 spores/ml) of the fungus and incubated for 30 hours at high humidity and a temperature of 23°C. Incubation is then continued at normal humidity and 22°C to 23°C.

Evaluation of protective action is made 7 to 8 days after infection and is based on fungus infestation.

b) After a cultivation period of 2 weeks, cucumber plants are treated by soil application with a spray mixture prepared from a wettable powder formulation of the test compound (concentration: 20 ppm, based on the volume of the soil). After 72 hours, the plants are infected with a spore suspension (1.5×10^5 spores/ml) of the fungus and incubated for 30 hours at high humidity and a temperature of 23°C. Incubation is then continued at normal humidity and 22°C.

Evaluation of protective action is made 7 to 8 days after infection and is based on fungus infestation.

Compounds of the Tables exhibit good activity in tests (a) and (b) and reduce fungus infestation to 0 tc 20 %. On the other hand, Colletotrichum infestation is 90 % on untreated and infected control plants.

c) Comparison test: Direct action against Colletotrichum lagenarium

The formulated active ingredient is mixed in various concentrations (100, 10, 1, 0.1 ppm) with autoclaved and cooled nutrient medium containing 10 000 spores per ml and is poured into microtitre plates. Incubation is then carried out at 22°C in the dark. After 2 to 3 days, fungus growth is measured by spectrophotometry.

With compounds of the Tables, no inhibition of fungus growth is observed; on the other hand, when the fungicide "Benomyl" (commercial product) is used as comparison substance at 0.2 ppm, 50 % inhibition (EC_{50}) of fungus growth occurs.

Example B.2: Action against Phytophthora infestans on tomato plants

a) After a cultivation period of 3 weeks, tomato plants are sprayed with a spray mixture prepared from a wettable powder formulation of the test compound (0.02 % active ingredient). After 72 hours, the treated plants are infected with a sporangia suspension of the fungus. Fungus infestation is evaluated after incubation of the infected plants for 5 days at 90-100 % relative humidity and 20°C.

Compounds of the Tables exhibit good activity in the tests and reduce fungus infestation to 0 to 20 %. On the other hand, Phytophthora infestation is 60 % on untreated and infected control plants.

Example B.3: Action against Pyricularia oryzae on rice plants

2-week-old rice plants are watered with a spray mixture prepared from a wettable powder formulation of the test compound (0.006 % active ingredient, based on the volume of the soil). The pots are then filled with water until the lowermost parts of the stems of the rice plants are standing in water. After 96 hours, the treated rice plants are infected with a conidia suspension of the fungus. Fungus infestation is evaluated after incubation of the infected plants for 5 days at 95-100 % relative humidity and approximately 24°C.

In comparison with untreated control plants (100 % infestation), fungus infestation on rice plants treated with a spray mixture comprising a compound of the Tables as active ingredient is only approximately 50 %.

Example B.4: Action against Cercospora nicotina on tobacco plants

a) Foliar application

Tobacco plants (8 weeks old) are sprayed with a formulated solution of the test compound (concentration: 0.02 % active ingredient). Four days after treatment, the plants are inoculated with a sporangia suspension of Cercospora nicotina (150 000 spores/ml), kept for 5 days in the dark at 25°C and high humidity and then incubated further under a normal day/night sequence.

Evaluation of the symptoms in the tests is based on the leaf surface infested with fungus. Infestation is approximately 60 % on the control plants; on plants treated with compounds of the Tables, infestation is 0 to 30 %.

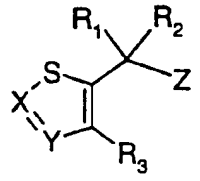
Example B.5: Action against Erysiphe graminis on wheat

Protective action: 18-day-old wheat plants are sprayed with a formulated solution of the test compound (0.02 % active ingredient). Immediately after the treatment the plants are incubated under cylinders. 24 hours later, the plants are covered. After a further 3 days, the treated plants are cut off above the primary leaf. The primary leaves are arranged horizontally and are inoculated in a dusting bell with Erysiphe graminis spores (spore density: 0.2 mg/m^2). The test is carried out in a climatic chamber with 12 hours of light (18 KLux), at 20°C and 12 hours of darkness, at 18°C. Infestation is evaluated 9 and 13 days after inoculation.

Compounds of the Tables exhibit good activity in the tests and reduce fungus infestation to 0 to 20 %. On the other hand, Erysiphe infestation is 70 % on untreated and infected control plants.

Claims

1. A process for protecting and immunizing plants against attack by phytopathogenic microorganisms which comprises applying a compound of formula I as active ingredient to the plants, to parts of the plants and/or to the locus of the plants



I

wherein

a) X is CR_4 and Y is N; or

b) X is N and Y is CR_5; or

c) X and Y are N; and wherein

Z is a C_1-group to which 1-3 halogen atoms or 1-3 unsubstituted or substituted hetero atoms selected from the group O, S and N are bonded;

R_1 and R_2 are independently H, OH, SH, CN, COOH, NO_2, NH_2, halogen, C_1-C_6alkyl, haloC_1-C_6alkyl, alkoxyC_1-C_6alkyl, aminoC_1-C_6alkyl, alkoxaminoC_1-C_6alkyl, C_1-C_6alkoxy, halo-C_1-C_6alkoxy, C_1-C_6alkanoyloxy, aroyloxy, C_1-C_6alkoxycarbonyl, aryloxycarbonyl, benzyloxy-carbonyl, C_1-C_6alkylcarbonyl, arylcarbonyl, benzylcarbonyl, aminocarbonyl, C_1-C_6alkylamino-carbonyl, C_1-C_6dialkylaminocarbonyl, C_1-C_6alkylthio, haloC_1-C_6alkylthio, C_1-C_6alkylsulfinyl, haloC_1-C_6alkylsulfinyl, C_1-C_6alkylsulfonyl, haloC_1-C_6alkylsulfonyl, arylsulfinyl, arylsulfonyl, C_2-C_6alkenyl, haloC_2-C_6alkenyl, C_2-C_6alkinyl, carboxyC_1-C_6alkyl, alkoxycarbonylC_1-C_6alkyl, haloalkoxycarbonylC_1-C_6alkyl, C_3-C_6cycloalkyl, alkanoylC_1-C_6alkyl, alkylcarbonyloxy-C_1-C_6alkyl, phenylcarbonyloxyC_1-C_6alkyl, C_1-C_6alkylamino, C_1-C_6dialkylamino, C_2-C_6alkenylamino, C_1-C_6alkanoylamino, C_1-C_6alkoxycarbonylamino, benzylamino, benzoylamino, benzyloxyarbonylamino, phenyl, phenoxy, benzyl or phenethyl, wherein all the aromatic groups are unsubstituted or substituted from 1 to 5 substituents independently selected from halogen, hydroxy, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy and nitro; or optionally substituted heterocyclyl; or tri(C_1-C_6alkyl)silyl or tri(C_1-C_6alkyl)silyloxy; with the proviso that R_1 and R_2 are not simultaneously a group selected from OH, SH, NO_2, NH_2, C_1-C_6alkylamino, C_1-C_6dialkylamino and C_2-C_6alkenylamino; or

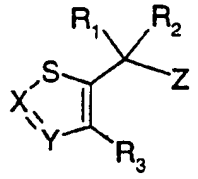
R_1 and R_2 together are =O or =S; or

R_1 and R_2 together with the carbon atom to which they are bonded are an unsubstituted or substituted 3 to 8 membered isocyclic or heterocyclic ring; or

R_2 and Z together with the carbon atom to which they are bonded are an unsubstituted or substituted 3 to 7 membered lactone, lactame, thiolactone or thiolactame, which ring may have 1 to 2 additional hetero atoms selected from the group O, S and N;

R_3, R_4 and R_5 are independently H, OH, SH, CN, NO_2, NH_2, halogen, C_1-C_6alkyl, halo-C_1-C_6alkyl, hydroxyC_1-C_6alkyl, alkoxyC_1-C_6alkyl, aminoC_1-C_6alkyl, alkoxaminoC_1-C_6alkyl, C_1-C_6alkoxy, C_1-C_6alkylthio, haloC_1-C_6alkylthio, C_1-C_6alkylsulfinyl, haloC_1-C_6alkylsulfinyl, C_1-C_6alkylsulfonyl, haloC_1-C_6alkylsulfonyl, halo-C_1-C_6alkoxy, C_2-C_6alkenyl, haloC_2-C_6alkenyl, C_2-C_6alkinyl, carboxyC_1-C_6alkyl, C_1-C_6alkanoyl, C_1-C_6alkoxycarbonyl, alkoxycarbonyl-C_1-C_6alkyl, haloalkoxycarbonylC_1-C_6alkyl, C_3-C_6cycloalkyl, alkanoylC_1-C_6alkyl, alkylcarbonyloxyC_1-C_6alkyl, phenylcarbonyloxyC_1-C_6alkyl, C_1-C_6alkylamino, C_1-C_6dialkylamino, C_2-C_6alkenylamino, C_1-C_6alkanoylamino, C_1-C_6alkoxycarbonylamino, benzylamino, benzoylamino, phenyl, phenoxy, benzyl or phenethyl, the phenyl rings of which are unsubstituted or substituted from 1 to 3 substituents independently selected from halogen, hydroxy, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy and nitro; or optionally substituted heterocyclyl.

2. A compound of formula I



I

wherein

a) X is CR_4 and Y is N; or

b) X is N and Y is CR_5; or

c) X and Y are N; and wherein

Z is a C_1-group to which 1-3 halogen atoms or 1-3 unsubstituted or substituted hetero atoms selected from the group O, S and N are bonded;

R_1 and R_2 are independently H, OH, SH, CN, COOH, NO_2, NH_2, halogen, C_1-C_6alkyl, haloC_1-C_6alkyl, alkoxyC_1-C_6alkyl, aminoC_1-C_6alkyl, alkoxaminoC_1-C_6alkyl, C_1-C_6alkoxy, halo-

C_1-C_6alkoxy, C_1-C_6alkanoyloxy, aroyloxy, C_1-C_6alkoxycarbonyl, aryloxycarbonyl, benzyloxycarbonyl, C_1-C_6alkylcarbonyl, arylcarbonyl, benzylcarbonyl, aminocarbonyl, C_1-C_6alkylaminocarbonyl, C_1-C_6dialkylaminocarbonyl, C_1.C_6alkylthio, haloC_1-C_6alkylthio, C_1-C_6alkylsulfinyl, haloC_1-C_6alkylsulfinyl, C_1-C_6alkylsulfonyl, haloC_1-C_6alkylsulfonyl, arylsulfinyl, arylsulfonyl, C_2-C_6alkenyl, haloC_2-C_6alkenyl, C_2-C_6alkinyl, carboxyC_1-C_6alkyl, alkoxycarbonylC_1-C_6alkyl, haloalkoxycarbonylC_1-C_6alkyl, C_3-C_6cycloalkyl, alkanoylC_1-C_6alkyl, alkylcarbonyloxyC_1-C_6alkyl, phenylcarbonyloxyC_1-C_6alkyl, C_1-C_6alkylamino, C_1-C_6dialkylamino, C_2-C_6alkenylamino, C_1-C_6alkanoylamino, C_1-C_6alkoxycarbonylamino, benzylamino, benzoylamino, benzyloxyarbonylamino, phenyl, phenoxy, benzyl or phenethyl, wherein all the aromatic groups are unsubstituted or substituted from 1 to 5 substituents independently selected from halogen, hydroxy, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy and nitro; or optionally substituted heterocyclyl; or tri(C_1-C_6alkyl)silyl or tri(C_1-C_6alkyl)silyloxy;

with the proviso that R_1 and R_2 are not simultaneously a group selected from OH, SH, NO_2, NH_2, C_1-C_6alkylamino, C_1-C_6dialkylamino and C_2-C_6alkenylamino; or

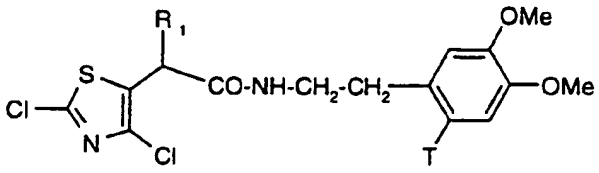
R_1 and R_2 together are =O or =S; or

R_1 and R_2 together with the carbon atom to which they are bonded are an unsubstituted or substituted 3 to 8 membered isocyclic or heterocyclic ring; or

R_2 and Z together with the carbon atom to which they are bonded are an unsubstituted or substituted 3 to 7 membered lactone, lactame, thiolactone or thiolactame, which ring may have 1 to 2 additional hetero atoms selected from the group O, S and N;

R_3, R_4 and R_5 are independently H, OH, SH, CN, NO_2, NH_2, halogen, C_1-C_6alkyl, haloC_1-C_6alkyl, hydroxyC_1-C_6alkyl, alkoxyC_1-C_6alkyl, aminoC_1-C_6alkyl, alkoxaminoC_1-C_6alkyl, C_1-C_6alkoxy, C_1-C_6alkylthio, haloC_1-C_6alkylthio, C_1-C_6alkylsulfinyl, haloC_1-C_6alkylsulfinyl, C_1-C_6alkylsulfonyl, haloC_1-C_6alkylsulfonyl, halo-C_1-C_6alkoxy, C_2-C_6alkenyl, haloC_2-C_6alkenyl, C_2-C_6alkinyl, carboxyC_1-C_6alkyl, C_1-C_6alkanoyl, C_1-C_6alkoxycarbonyl, alkoxycarbonylC_1-C_6alkyl, haloalkoxycarbonylC_1-C_6alkyl, C_3-C_6cycloalkyl, alkanoylC_1-C_6alkyl, alkylcarbonyloxyC_1-C_6alkyl, phenylcarbonyloxyC_1-C_6alkyl, C_1-C_6alkylamino, C_1-C_6dialkylamino, C_2-C_6alkenylamino, C_1-C_6alkanoylamino, C_1-C_6alkoxycarbonylamino, benzylamino, benzoylamino, phenyl, phenoxy, benzyl or phenethyl, the phenyl rings of which are unsubstituted or substituted from 1 to 3 substituents independently selected from halogen, hydroxy, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy and nitro; or optionally substituted heterocyclyl;

with the exception of the compounds of the formula



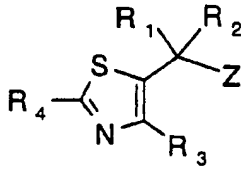
wherein

a) R_1 is $OCO-CH_3$ and T is Br,

b) R_1 is OH and T is Br,

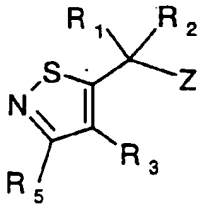
c) R_1 is OH and T is H.

3. A compound according to claim 2 of formula I.A



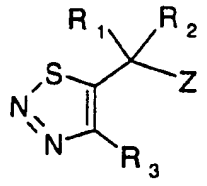
I.A.

4. A compound according to claim 2 of formula I.B



I.B.

5. A compound according to claim 2 of formula I.C



I.C.

6. A compound according to claim 2 wherein

Z is CN, CO-A, CS-A or $CH(OR_{10})_2$;

A is hydrogen, halogen, OR_6, SR_7, $N(R_8)R_9$, $ON(R_{11})R_{12}$ or $N(R_{13})OR_{14}$;

R_6 to R_{14} are independently hydrogen, an unsubstituted or substituted, open-chained, saturated or unsaturated hydrocarbon radical containing up to 8 carbon atoms, an unsubstituted or substituted, cyclic, saturated or unsaturated hydrocarbon radical containing up to 10 carbon atoms, unsubstituted or substituted benzyl or phenethyl, an unsubstituted or substituted acyl group containing up to 8 carbon atoms, an unsubstituted or substituted benzoyl group, or an unsubstituted or substituted heterocyclyl radical; or

R_8 and R_9, or R_{11} and R_{12}, together with the nitrogen atom to which they are bonded, form a 5- or 6-membered, unsubstituted or substituted heterocycle having 1 to 3 hetero atoms selected from O, S and/or N;

R_{10} are identical or different and are C_1-C_6alkyl that is unsubstituted or substituted by phenyl, C_1-C_2alkoxy, phenoxy or by benzyloxy; or

two substituents OR_{10}, together with the carbon atom to which they are bonded, form a cyclic acetal group that is unsubstituted or substituted by C_1-C_3alkyl, phenyl, benzyl, hydroxy or by C_1-C_3hydroxyalkyl.

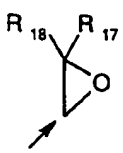
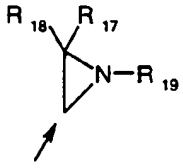
7. A compound according to claim 2 wherein

R_1 is H, OH, NH_2, halogen, COOH, C_1-C_4alkyl, haloC_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4alkanoyloxy, aroylyloxy, C_1-C_4alkoxycarbonyl, aryloxycarbonyl, benzyloxycarbonyl, C_1-C_4alkylcarbonyl, arylcarbonyl, benzylcarbonyl, aminocarbonyl, C_1-C_4alkylaminocarbonyl, C_1-C_4dialkylaminocarbonyl, alkanoylC_1-C_4alkyl, alkylcarbonyloxyC_1-C_4alkyl, C_2-C_4alkenyl, haloC_2-C_4alkenyl, C_1-C_4alkylamino, C_1-C_4dialkylamino, C_1-C_4alkanoylamino, C_1-C_4alkoxycarbonylamino, benzylamino, benzoylamino, phenyl, phenoxy, benzyl or phenethyl, the phenyl rings of which are unsubstituted or substituted from 1 to 3 substituents

independently selected from halogen, hydroxy, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy and nitro;

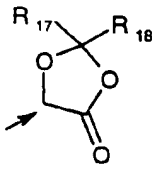
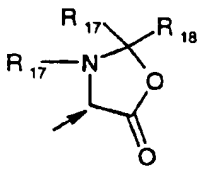
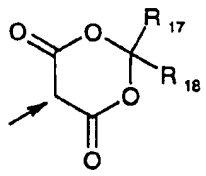
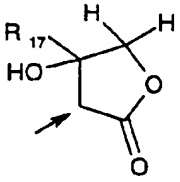
R_2 is H, OH, C_1-C_4alkyl, C_1-C_4alkoxy or phenyl; or

R_1 and R_2 together are a group selected from

or

R_2+Z together are a group selected from

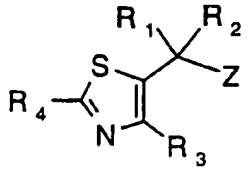





wherein R_{17}, R_{18} and R_{19} are independently H or C_1-C_4alkyl;

R_3 is H, halogen, C_1-C_6alkyl, haloC_1-C_6alkyl, C_3-C_6-cycloalkyl, C_1-C_4 alkoxycarbonyl, phenyl which is unsubstituted or substituted from 1 to 3 substituents independently selected from halogen, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy, amino, C_1-C_4alkylamino, C_1-C_4dialkylamino, benzylamino, C_1-C_4alkanoylamino, benzoylamino, C_1-C_4alkoxycarbonylamino, formyl, or a 4-7-membered cyclic or C_1-C_4alkyl open-chained acetal or thioacetal thereof;

R_4 is H, OH, halogen, amino, C_1-C_6alkyl, C_1-C_4alkylamino, C_1-C_4alkenylylamino, C_1-C_4dialkylamino, benzylamino, C_1-C_4alkanoylamino, benzoylamino, C_1-C_4alkoxycarbonylamino.

8. A compound according to claim 3 of formula I.A



I.A

wherein

Z is CO-A;

A is hydrogen, OR_6, SR_7, $N(R_8)R_9$;

R_1 is H, OH, halogen or C_1-C_4alkyl,

R_2 is H;

R_3 is H, OH, C_1-C_6alkyl, C_3-C_6cycloalkyl, haloC_1-C_6alkyl, C_1-C_6alkoxy or haloC_1-C_6alkoxy, formyl, or a 4-7-membered cyclic or C_1-C_4alkyl open-chained acetal or thioacetal thereof;

R_4 is Cl;

R_6, R_7, R_8 and R_9 are independently H, C_1-C_6alkyl, haloC_1-C_6alkyl, C_1-C_6alkoxy, haloC_1-C_6alkoxy, C_1-C_4alkoxycarbonyl, C_1-C_4alkanoylC_1-C_4alkyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkylmethyl, phenyl, benzyl, or phenethyl, the phenyl rings of which are unsubstituted or substituted from 1 to 3 substituents independently selected from halogen, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy.

9. A process for the preparation of a compound of formula I.1

II.1 I.1

wherein X, Y and R_3 are as defined for formula I,

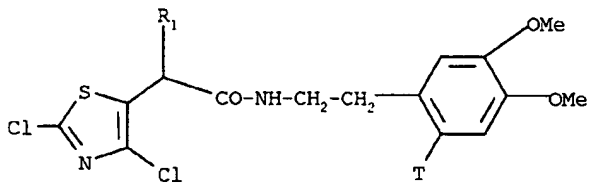
which comprises reaction of a compound of formula II.1 with carbon monoxide under pressure of 2-20 bars in presence of a catalyst.

10. A composition for protecting and immunizing plants against attack by microorganisms, comprising a compound of formula I of claim 1 together with a suitable carrier.

AMENDED CLAIMS

[received by the International Bureau on 09 June 1999 (09.06.99);
original claims 2 and 10 amended; remaining claims unchanged (4 pages)]

A) with the exception of the compounds of the formula



wherein

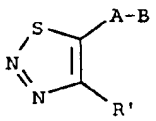
a) R_1 is $OCO-CH_3$ and T is Br,

b) R_1 is OH and T is Br,

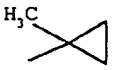
c) R_1 is OH and T is H;

and

B) with the exception of thiadiazole derivatives having the formula



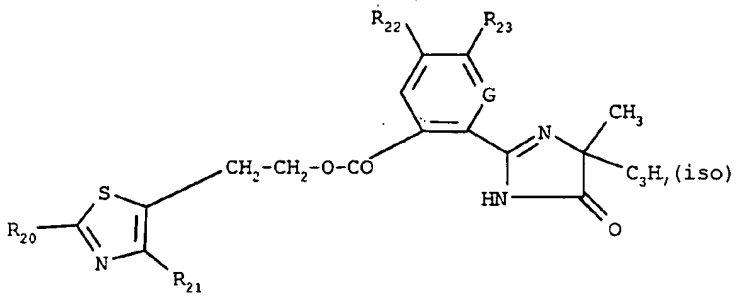
wherein R' is methyl or phenyl,

A is CH_2, CHCl, $CHCH_3$, $C(CH_3)_2$, $CH-C_6H_5$,  , and

B is CHO, CN, COOH, $COOCH_3$, $COOC_2H_5$, $COOC_3H_7$(iso), $COOC_8H_{17}$(n), $COOCH_2CH=CH_2$, $CONH_2$, $CONHCH_3$, $CONHC_3H_7$(iso), $CON(CH_3)_2$, pyrrolidinoyl, morpholinoyl, 4-methoxicarbonyl-piperazinoyl, 4-oxo-piperidinoyl, $CH(SCH_3)(SOCH_3)$, $CONH-C_6H_4-OCH_3$(4) or $CON(CH_3)C_6H_5$;

and

C) with the exception of thiazolyl derivatives having the formula



wherein

R_{20} is hydrogen, CH_3, C_2H_5,

R_{21} is hydrogen, CH_3, C_2H_5,

R_{22} is hydrogen, C_1-C_3alkyl, n-C_4H_9, Cl or Br,

R_{23} is hydrogen, CH_3, C_2H_5, or

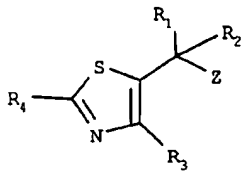
R_{22} and R_{23} together with the ring to which they are attached form a condensed six-membered carbocyclic aromatic ring which may be monochlorinated, and

G represents CH or N;

and

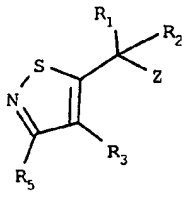
D) with the exception of 7-(1,2,3-thiadiazolyl-5-acetamido)-3-(5-methyl-1,3,4-thiadiazol-2-ylthiomethyl)-3-cephem-4-carboxylic acid.

3. A compound according to claim 2 of formula I.A

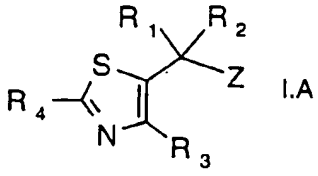


I.A.

4. A compound according to claim 2 of formula I.B.



I.B.



I.A

wherein

Z is CO-A;

A is hydrogen, OR_6, SR_7, $N(R_8)R_9$;

R_1 is H, OH, halogen or C_1-C_4alkyl,

R_2 is H;

R_3 is H, OH, C_1-C_6alkyl, C_3-C_6cycloalkyl, haloC_1-C_6alkyl, C_1-C_6alkoxy or haloC_1-C_6alkoxy, formyl, or a 4-7-membered cyclic or C_1-C_4alkyl open-chained acetal or thioacetal thereof;

R_4 is Cl;

R_6, R_7, R_8 and R_9 are independently H, C_1-C_6alkyl, haloC_1-C_6alkyl, C_1-C_6alkoxy, haloC_1-C_6alkoxy, C_1-C_4alkoxycarbonyl, C_1-C_4alkanoylC_1-C_4alkyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkylmethyl, phenyl, benzyl, or phenethyl, the phenyl rings of which are unsubstituted or substituted from 1 to 3 substituents independently selected from halogen, C_1-C_4alkyl, halo-C_1-C_2alkyl, C_1-C_2alkoxy, halo-C_1-C_2alkoxy.

9. A process for the preparation of a compound of formula I.1

II.1 I.1

wherein X, Y and R_3 are as defined for formula I,

which comprises reaction of a compound of formula II.1 with carbon monoxide under pressure of 2-20 bars in presence of a catalyst.

10. A composition for protecting and immunizing plants against attack by microorganisms, comprising a compound of formula I of claim 2 together with a suitable carrier.

STATEMENT UNDER ARTICLE 19

The amendments effected in claim 2 will restore the novelty by way of disclaimer. They take the following references of the International Search Report into account:

- WO 98 14437 A (NIHON NOHYAKU Co., Ltd.)
  Examples 307 to 321, 325, 327 to 331, 335, 336, 347, 383, 384 and 385 (identical to 422); [disclaimer B]
- DE 19 53 861 A (Fujisawa Pharmaceutical Co. Ltd.)
  Example 16, which is identical to DE 22 62 262, example 65; [disclaimer D]
- DE 22 62 262 A (Fujisawa Pharmaceutical Co. Ltd.)
  Example 65, which is identical to DE 19 53 861 A, example 16; [disclaimer D]
- EP 0 213 079 A (Ciba-Geigy AG)
  Compounds Nos. 1.01 to 1.22, 1.50 to 1.54, 3.01 to 3.22, 3.58 and 3.59. [disclaimer C]

INTERNATIONAL SEARCH REPORT

Ir. ational Application No
PCT/EP 98/08335

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D277/32 C07D277/30 C07D275/02 C07D285/06 C07D417/04
A01N43/78 A01N43/74 A01N43/82

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 17840 A (AGREVO UK LTD.) 13 June 1996 cited in the application see page 20, compounds no. 39, 40, 41 see claims 1,3,4	1-3,6-8, 10
P,X	WO 98 14437 A (NIHON NOHYAKU CO., LTD.) 9 April 1998 see examples no. 325,335,336,384,385,422 see abstract	1,2,5,6, 10
X	DE 19 53 861 A (FUJISAWA PHARMACEUTICAL CO. LTD.) 6 May 1971 see example 16	2,5
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 April 1999	16/04/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hass, C

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INTERNATIONAL SEARCH REPORT

Im ational Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 213 079 A (CIBA-GEIGY AG) 4 March 1987 see table 1, compounds no. 1.01 to 1.22 and 1.50 to 1.54; table 3, compounds no. 3.01 to 3.22 and 3.58 and 3.59	2,3
A	EP 0 395 174 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B. V.) 31 October 1990 cited in the application see claims 1,6,8,10	1,2,10
A	WO 96 29871 A (NIHON NOHYAKU CO., LTD.) 3 October 1996 cited in the application see claims 1,10; table 1	1,2,10
A	WO 97 20465 A (BAYER AG) 12 June 1997 cited in the application see claims 1,3,4,6,7	1,2,10
A	EP 0 757 987 A (NISSAN CHEMICAL INDUSTRIES, LTD.) 12 February 1997 cited in the application see claims 1,4	1,2,10
A	US 5 135 927 A (W. TÖPFL ET AL.) 4 August 1992 cited in the application see the whole document	1,2,10

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